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THE REARRANGEMENT OF 4,4-DIPHENYLCYCLOHEXA-2,5-DIENYLIDENE

PETER K. FREEMAN* and KARL E. SWENSON
Department of Chemistry, Oregon State University, Corvallis, OR 97331, U.S.A.

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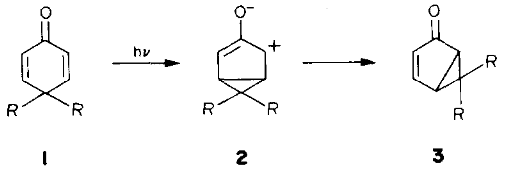
Abstract—Pyrolytic decomposition of the Li salt of the tosylhydrazone of 4,4-diphenyl-2,5-cyclohexadienone produces a mixture of biphenyl, *o*-terphenyl, *p*-terphenyl, methyl-*o*-terphenyl and the azine of 4,4-diphenyl-2,5-cyclohexadienone (**13**). Insight into the reaction pathway was provided by the pyrolytic decomposition of 2-deuterio tosylhydrazone **8a** which generates *o*-terphenyl **10a** and **10b** in a ratio of 69:31. These results are interpreted in terms of the carbene rearrangements of Schemes 2, 3 and 5.

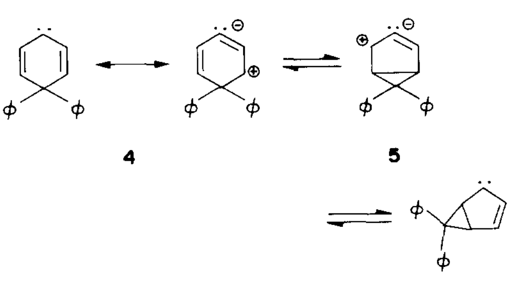
One of the most intensively studied photochemical rearrangements is that of the 2,5-cyclohexadienone system (**1**) to the bicyclo[3.1.0]hex-3-en-2-one skeleton (**3**) (eqn 1).[1] Evidence has been developed for a sequence of steps that include zwitterion **2** as a key intermediate.[2]



(1)

1 **2** **3**

It appeared to us that there are some interesting similarities between this photochemical rearrangement and the prospects which might be anticipated for an analogous carbene species. For example carbene **4** might be expected to undergo an allylcarbinyl–cyclopropylcarbinyl rearrangement to generate zwitterion **5**, which could undergo a 1,4-sigmatropic shift to produce bicyclic bivalent **6**. The prospect for observation of a unique carbene to carbene rearrangement and the opportunity to compare 4,4-diphenylcyclohexadienylidene with previously explored dialkyl analogs[3,4] prompted our study of carbene **4**.

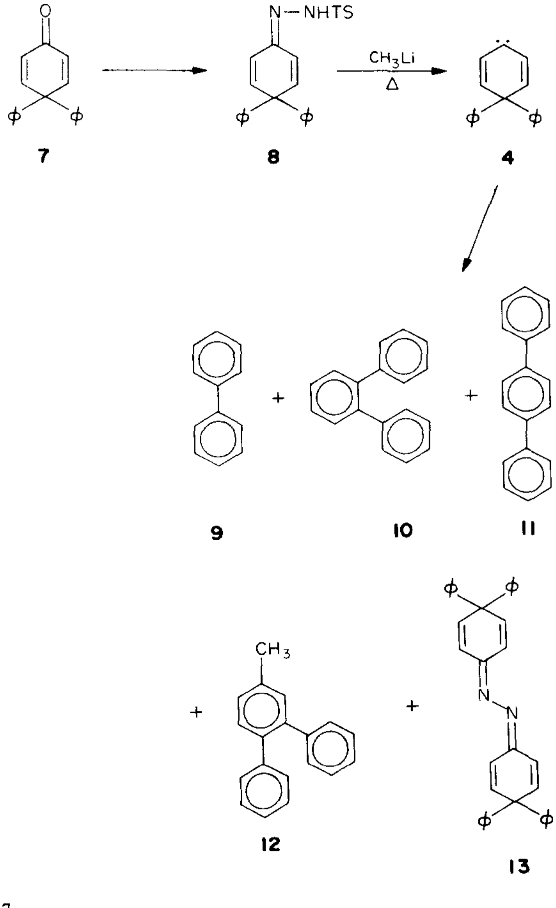


4 **5**

(2)

6

The synthesis of ketone **7** was accomplished according to the method of Zimmerman *et al.*[5] Conversion of **7** to the tosylhydrazone **8** was performed with tosylhydrazine in refluxing methanol with no complications. The tosylhydrazone was converted to its Li salt with MeLi and decomposed as the dry salt at 118–185°. Separation on a silica gel column monitored by TLC gave an early eluting fraction which was analyzed by VPC. The major product (51%) of the reaction, eluting second from the silica gel column, was a yellow solid identified as 4,4-diphenyl-2,5-cyclohexadienone azine by spectral comparison with a sample of azine **13** prepared by reaction of ketone **7** with hydrazine. Analysis by VPC of the early eluting fraction on a silica gel column gave five major components. Biphenyl **9**, O-terphenyl **10**, and *p*-terphenyl **11**, identified by comparison of their VPC retention times, NMR spectra, and mass spectra with authentic samples, were present in a per cent composition ratio of 24.8:46.7:9.2. The fourth component gives NMR and mass spectra consistent with its being a Me substituted *o*-terphenyl **12** (5.8%) while the fifth, component (13.4%) remains unidentified. The total yield for the VPC volatile components was 6.4%. A non-volatile high mol wt residue was isolated from the silica gel column which accounted for a further 17% of the reactant.

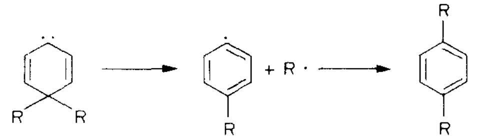


7 **8** **4**

9 **10** **11**

12 **13**

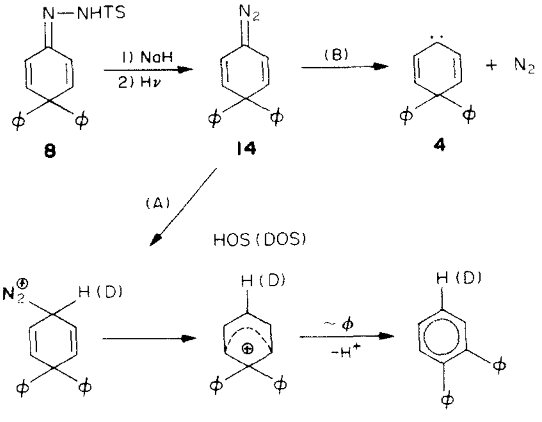
Azines are commonly found products of the reaction of a carbene with a diazo compound.[6a] A number of possible pathways for their formation exist. No attempt was made to study the details of the formation of **13**. Biphenyl (**9**) and *p*-terphenyl (**11**) most probably arise by the radical mechanism proposed for the 4,4-dialkyl analogs by Jones *et al.*[3] (eqn 3).



(3)

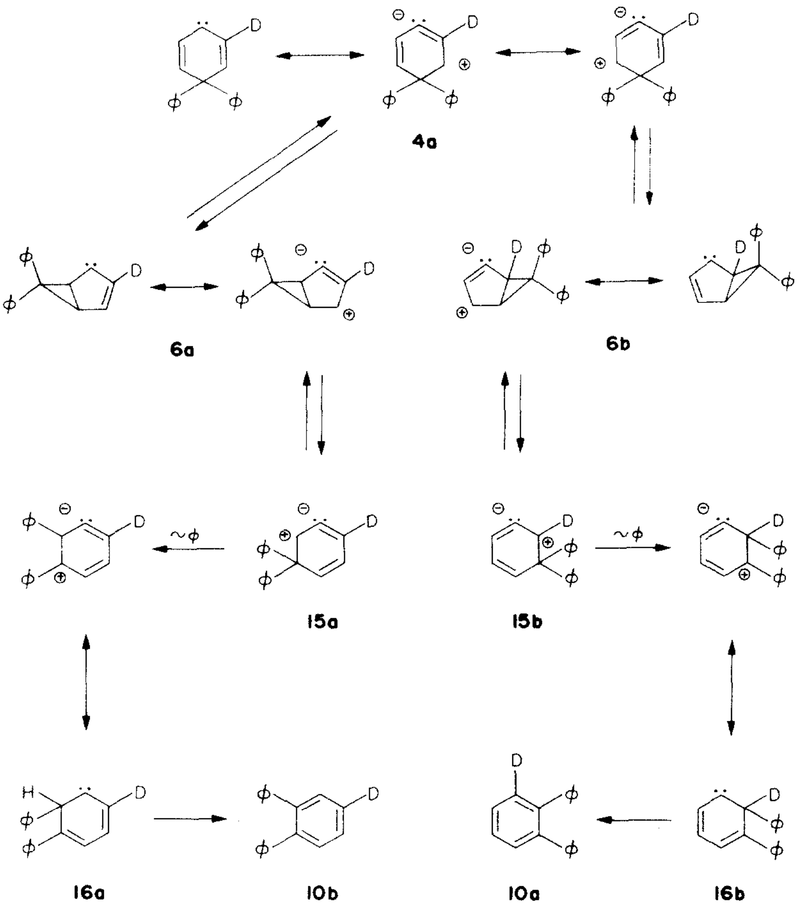
The Me group on Me substituted terphenyl **12** is possibly derived from a small amount of methyl bromide present in the MeLi, since photolysis of the Na salt of **8**, prepared by treating **8** with sodium hydride yields no methyl terphenyl **12**.

The major monomeric product of carbene **4** is O-terphenyl **10**. Its presence is of considerable interest in that no *ortho* products were isolated from the analogous 4,4-dialkylcyclohexadienylidenes.[3] Since considerable care was taken to assure that protic inpurities were not present in the pyrolytic decomposition of the Li salt of tosylhydrazone **8**, it is unlikely that the carbonium ion route (route A) outlined in Scheme 1 could be a significant contributor in competition with the carbene partway (route B). Even so, we felt it was reasonable to test the sensitivity of the decomposition of diazo compound **14** to the presence of protic impurities. Tosylhydrazone **8** was converted to its Na salt with sodium hydride and photolyzed in THF in the presence of one equivalent of deuterium oxide. After isolation by preparative VPC, **10** was analyzed by low voltage mass spectrometry, and, within experimental error, no deuterium $(0 \pm 1\%\ d_1)$ was found incorporated in the product. This provides evidence that even in the presence of small quantities of protic materials, **10** is formed from a carbene precursor under these conditions and most likely under the conditions of dry salt pyrolysis.



Scheme 1. **10**

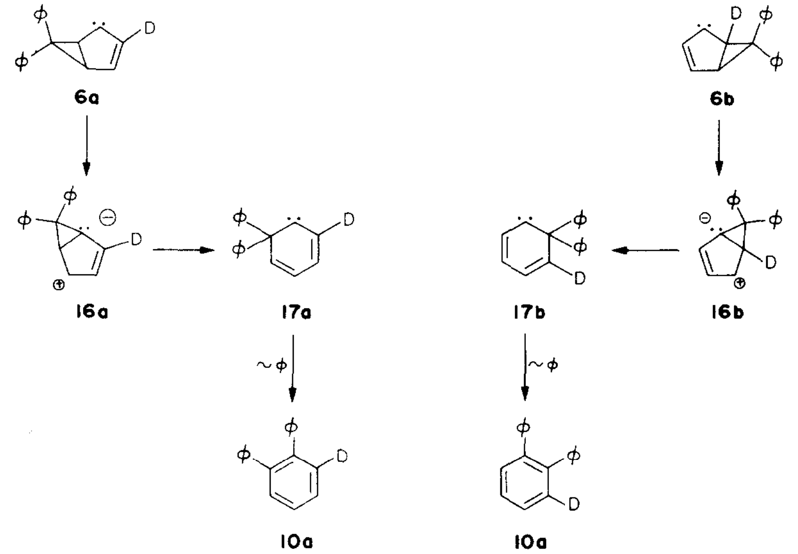
A rationale for the generation of *o*-terphenyl from bivalent **4** may be provided by expanding the carbene to carbene rearrangement pictured in eqn (2) (Scheme 2).



Scheme 2.

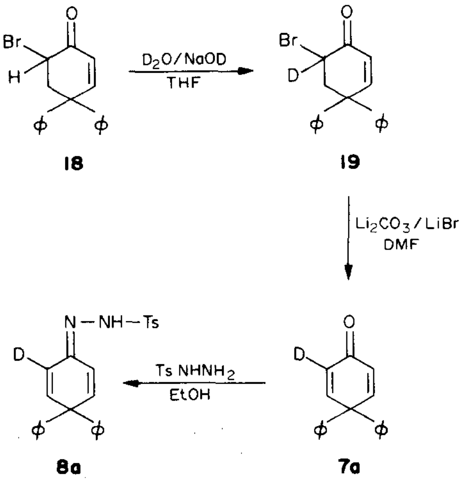
Monodeuterio diphenylcyclohexadienylidene (**4a**) in this sequence rearranges to bicyclic carbene **6a** (or **6b**). A cyclopropylcarbinyl to allylcarbinyl ring cleavage produces **15a** (**15b**), which with a 1,2-phenyl shift generates carbene **16a** (**16b**). Hydrogen (deuterium) migration leads to *o*-terphenyl with equal proportions of **10b** and **10a**.

Alternatively bicyclic carbene **6a** (**6b**) might undergo a 1,4 suprafacial alkyl shift producing **16a** (**16b**), which with cyclopropylcarbinyl to allylcarbinyl cleavage generates carbene **17a** (**17b**) (Scheme 3). Phenyl migration in either labeled form results in *o*-terphenyl with the label solely in the *ortho* (3) position (**10a**). The alkyl migration (**6**→**16**) and 1,2-phenyl migration (**17**→**10a**) to a carbene center featured in this sequence are supported by examples in Refs. 6*b* and 7.



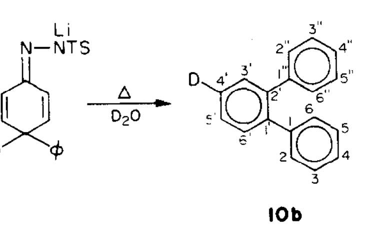
Scheme 3.

It seemed appropriate, therefore, at this point in our study, to employ a D label at C-2 in the starting tosylhydrazone. Zimmerman's synthesis of the starting ketone **7** was modified to introduce D as outlined in Scheme 4. Bromoenone **18** was treated with D_2O/NaOD in THF to give the deuterated bromoenone **19** (d of d at δ 4.55 for HBrC now missing). Reaction of **19** with lithium carbonate–lithium bromide yielded **7a** (29.9 ± 1.2 d_0, 68.8 ± 1.7 d_1 and 1.3 ± 1.1 %d_2) which was converted to the tosylhydrazone **8a** with tosylhydrazine in ethanol. As a check on the persistence of D label through tosylhydrazone and Li salt of tosylhydrazone formation, tosylhydrazone **8a** was converted to the corresponding Li salt and subjected to pyrolysis (diglyme/H_2O) to produce *o*-terphenyl (27.8 ± 0.8 d_0, 72.6 ± 0.8 d_1, 0 ± 0.34 d_2).



Scheme 4.

The tosylhydrazone **8a** was converted to its Li salt and pyrolyzed as the dry salt. The product distribution was similar to that obtained for the undeuterated case. The *o*-terphenyl was isolated and D incorporation determined by low voltage mass spectrometry. The D distribution was determined using a combination of ^{13}C NMR and mass spectrometry.[8] Figure 1 shows the ^{13}C NMR spectrum of undeuterated *o*-terphenyl. All seven different C atoms are resolved. The assignments made were verified by preparation of *o*-terphenyl with D substituted at C-4′ (eqn 4). Comparison of the ^{13}C NMR spectra of undeuterated *o*-terphenyl **10** and 4′-deuterio-*o*-terphenyl **10b** (Fig. 1) shows that upon incorporation of D at the 4′ position, the C absorbance for C-3′,6′ (130.47–130.57 ppm) is split into two peaks and the absorbance for C-4′,5′ (127.32) has decreased to one-half of its original intensity. Since the sample of **10b** used is monodeuterated (>98%), the C atom at 4′ apparently does not give rise to a ^{13}C NMR signal.[9] What is observed is the C atom 5′ and thus, the intensity of this NMR signal is reduced to one-half.



(4)

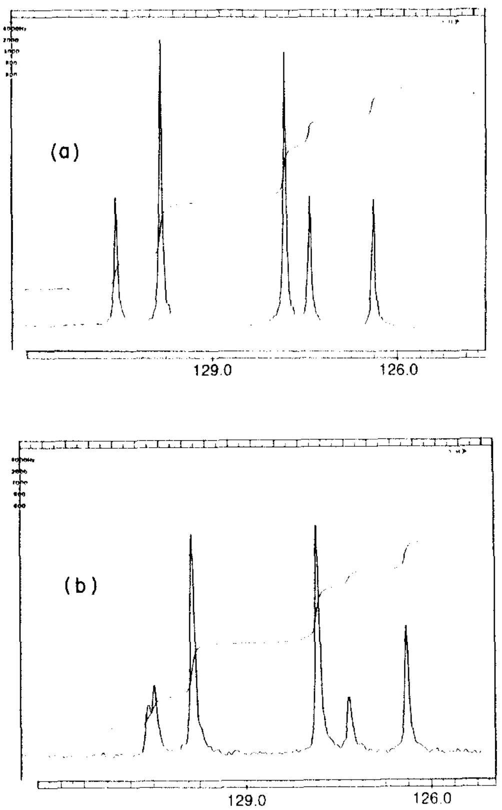
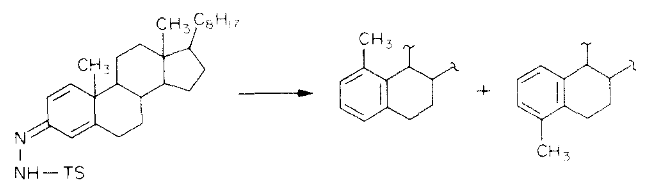


Fig. 1. Carbon-13 NMR spectra of (a) *o*-terphenyl (**10**) and (b) 4′-deuterio-*o*-terphenyl (**10b**). The ipso carbons are off scale downfield.

In addition, the signal assigned to C-5′ in **10b** is 0.11 ppm upfield from the C-4′,5′ signal of undeuterated *o*-terphenyl, in agreement with the predicted geminal (^{13}CCD)[10] isotope effect. This D isotope effect also explains the two signals for C-3′ and C-6′. The downfield absorbance (130.57 ppm) is assigned to C-6′ as it has the same chemical shift as the C-3′,6′ signal of undeuterated *o*-terphenyl. The peak shifted upfield by 0.10 ppm is C-3′ as would be expected from the presence of the geminal D atom.

Using the C-4, C-4″ signal at 126.37 ppm as a reference, the D distribution was 69 ± 8.8% **10a** to 31 ± 8.8% **10b**. Clearly neither Scheme 2 or 3 alone may be employed as the mechanistic rationale; however, a combination of the two fits very nicely. Carbene to carbene rearrangement to bicyclic carbene **6a** is followed by competing cyclopropylcarbinyl to allylcarbinyl ring cleavage to **15** and 1,4-sigmatropic alkyl shift to **16**. Even though appealing, this particular mechanistic proposal must be expanded to include the insight provided by the study of Dannenberg and Gross,[11] who found that carbenoid decomposition of **20** gave two isomeric aromatic products **21** and **22** (eqn 5).



20 **21** **22** (5)

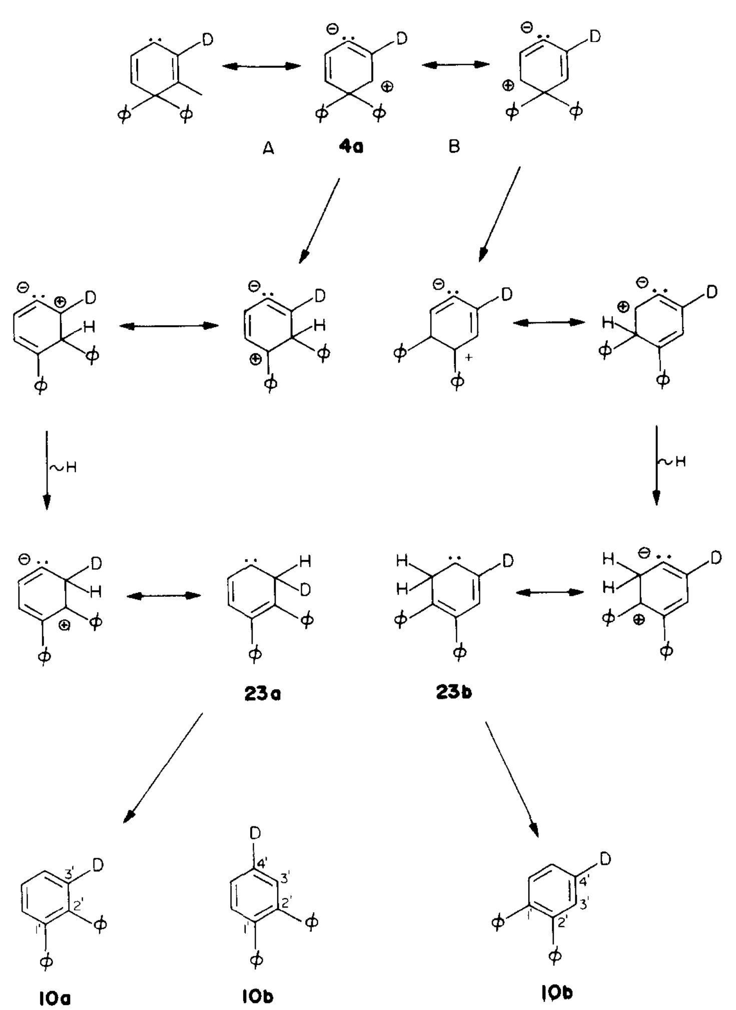
Building on their rationale we propose Scheme 5 as a third alternative. Consecutive phenyl and H-migrations generate carbene **23a** (**23b**). Carbene **23a** would be expected to exhibit an isotope effect in the final H-migration step. Isotope effects for H-migration in simple alkyl carbenes are in the range $k_H/k_D = 1.0$–1.4.[12] Consequently, using a range for $k_H/k_D = 1.0$–1.5, the predicted ratio for **10a**:**10b** is 25–30:70–75. Since the major product is **10a**, Scheme 5 could represent the reaction pathway to the minor component **10b**.

At this point it is of interest to consider whether the rearrangement of the carbene, related to **20**, to **21** and **22** could be more satisfactorily interpreted in terms of the mechanistic routes pictured in Schemes 2 and 3. Scheme 2 does provide a pathway to **21** but not to **22**. The bridging of one of the C-4 substituents in **20** would be expected, in fact, to inhibit the use of pathways in Schemes 2 and 3 which lead to strained bridged polycyclic intermediates. Different outcomes for carbenoid decomposition of **20** and **4** do not seem surprising. The rearrangement of the carbene generated from **20** to products **21** and **22** remains most economically explained by Scheme 5, while Scheme 5 can only dictate the reaction course to a minor extent for carbene **4a**. Alternatively participation of Scheme 2 to a major extent and Scheme 3 to a minor extent remains an attractive rationalization.

EXPERIMENTAL

M.ps were determined using a Büchi m.p. apparatus and are uncorrected. All b.ps are uncorrected. IR spectra were recorded on a Perkin–Elmer 727B IR spectrophotometer. P NMR spectra were recorded on a Varian Associates EM-360 (60 MHz) or HA-100 (100 MHz) spectrometer, while ^{13}C NMR spectra were run on a Varian Associates FT-80A spectrometer. Mass spectra were obtained on a Varian-Matt Ch-7 mass spectrometer interfaced to a System 150 data system. High resolution mass spectra were carried out by the University of Oregon Chemistry department. Elemental analyses were performed by Chemalytics, Inc., 2330 S. Industrial Park Dr., Tempe, Arizona. VPC analyses were carried out on an Aerograph A-90-P2 chromatograph equipped with a thermal conductivity detector. The following columns were used: (a) 6 ft × 0.25 in aluminum containing 7% OV-17 on Chromosorb P, 60/80 mesh; (b) 5 ft × 0.25 in aluminum containing 7% SE-30 on Chromosorb P, 60/80 mesh.

Preparation of 4,4-diphenyl-2,5-cyclohexadienone tosylhydrazone **8**. A soln of 5.037 g (20.5 mmol) of **7** in 50 mL MeOH was prepared in a 100 mL flask fitted with a magnetic stirrer and reflux condenser. It was necessary to warm the mixture to 50° to dissolve all the dienone. A soln of 3.812 g (20.5 mmol) tosylhydrazine in 10 mL MeOH (also warmed to 50°) was added to the dienone soln and this soln heated to 60° for 4 hr. Upon cooling, an off-white ppt formed and precipitation was completed by placing the reaction in the refrigerator overnight. The crude product was recrystallized from MeOH to afford 4.701 g (11.3 mmol, 55%) of the desired **8**; m.p. 140–141° dec; NMR (100 MHz, $CDCl_3$), δ7.90 (d, J = 8 Hz, 2H, tosyl aromatic protons), 7.22 (m, 12H, aromatic protons), 6.80 (broadened s, 2H, vinyl protons), 6.32 (d, J = 4 Hz, 2H, vinyl protons), 2.39 (s, 3H, aromatic Me protons); IR (Nujol mull), 3260 cm^{-1} (m), 1650 (w), 1595 (m), 1345 (s), 1160 (s). Chemical ionization mass spectrum.



Scheme 5.

Calc. for $C_{25}H_{22}N_2O_2S$: 414; positive ion 415, negative ion 413.

Dry salt pyrolysis of the lithium salt of 4,4-*diphenyl*-2,5-*cyclohexadienone tosylhydrazone* **8**. A 100 mL flask fitted with a magnetic stirrer, gas inlet, and septum was charged with 0.9386 g (2.265 mmol) of **8** dissolved in 20 mL anhyd. THF. The flask was thoroughly flushed with dry N_2 and 1.30 mL (2.28 mmol) 1.75 M MeLi was added via a syringe. Then an additional 0.3 mL (0.53 mmol) MeLi was added, just enough to produce a distinctive deep gold color presumed to be the dianion. A heavy white ppt formed and this suspension was stirred under N_2 at room temp. for 45 min. The THF was removed by blowing on the stirred suspension with a stream of dry N_2. When most of the THF had evaporated, the remainder was removed by pumping at 0.3 torr for 1 hr. The usual all glass decomposition apparatus was set up and the salt decomposed by heating to 185°. Nitrogen evolution began at 118° and heating was continued for ten minutes after nitrogen evolution had ceased. The volatile products which had been collected at −78° were washed from the traps with benzene. The residue in the decomposition flask was dissolved in 50 mL of benzene and combined with the benzene washes of the traps. The combined benzene extracts were washed six times with 75 mL of water and dried over magnesium sulfate. The benzene was removed on the rotary evaporator to leave a reddish-yellow oil. This oil was chromatographed on a 1.8 × 30 cm silica gel column (E. M. Reagents Silica Gel 60, 70/230 mesh) eluting with 200 mL of 90/10 hexane–dichloromethane, 100 mL of 70/30 hexane–dichloromethane, 100 mL of 60/40 hexane–dichloromethane, and finally 100 mL of methanol to remove the polar residue. The column fractions were analyzed by tlc (silica gel, dichloromethane) and combined into three fractions. The fraction with the largest R_f value was further analyzed by VPC (col. A, 210°, 70 mL/min) after removal of the solvent on the rotary evaporator. Five major volatile components with the following retention times and per cent composition were obtained: A(1.3 min, 24.8%), B(9.0 min, 46.7%), C(12.6 min, 5.8%), D(29.2 min, 9.2%), and E(41.0 min, 13.4%). Comparison of VPC retention times, NMR spectra, and mass spectra with available authentic samples was used to identify A as biphenyl, B as *o*-terphenyl, and D as *p*-terphenyl. Compound C has *m*/*e* 244 and NMR (80 MHz, $CDCl_3$), δ7.38 (s, 2H, aromatic protons), 7.20, 7.11 (s at 7.20 and two almost merged singlets at 7.11, total area 11H, aromatic protons), 2.40 (s, 3H, aromatic methyl). This has been tentatively identified as a Me substituted terphenyl. Compound E, *m*/*e* 244, NMR (80 MHz, $CDCl_3$), δ7.63–7.00 (three complex overlapping m in the aromatic region) remains unidentified. Anthracene was added as an internal standard and the yield of volatile product from this column fraction was found to be 6.4%. The second fraction (intermediate R_f) from the column chromatography was evaporated on the rotary evaporator to give 0.2791 g (0.572 mmol, 51%) of yellow-brown solid identified as 4,4-diphenyl-2,5-cyclohexadienone azine **13** by comparison of its NMR and mass spectra with those of an authentic compound. The third column fraction (R_f about 0.05) was evaporated and weighed to give 0.0887 g of uncharacterizable high molecular weight residue (17%).

Synthesis of 4,4-*diphenyl*-2,5-*cyclohexadienone azine* **13**. A 10 mL flask fitted with a magnetic stirrer was charged with 0.2296 g (0.933 mmol) of 4,4-diphenyl-2,5-cyclohexadienone **7** and

26.8 μl (27.5 mg, 0.4666 mmol) of 85% hydrazine hydrate in 10 mL of 95% ethanol. After the addition of one drop of concentrated hydrochloric acid, the reaction was allowed to stir for seven days. A brilliant yellow ppt formed, which was isolated to yield 0.1371 g (0.281 mmol, 60%) of azine **13** identified by its NMR and mass spectra; m.p. 231–233° dec.; NMR (100 MHz, $CDCl_3/CCl_4$), δ7.28 (s, 24H, aromatic and vinyl protons), 6.73, 6.66 (two d, J = 1 Hz, total of 4H, vinyl protons); IR (Nujol mull), 1665 cm^{-1} (s), 1600 (m), 1555 (m), 1038 (s), 830 (s), 760 (s), 705 (s).

High resolution mass spectrum. Calc. for $C_{36}H_{28}N_2$: 488.225. Found: 488.222.

Photolysis of the sodium salt of 4,4-*diphenyl*-2,5-*cyclohexadienone tosylhydrazone* **8** *in THF in the presence of deuterium oxide.* A 50 mL flask fitted with a magnetic stirrer and gas inlet was charged with 69.2 g (1.65 mmol) of a 57.2% sodium hydride dispersion in mineral oil. The sodium hydride was washed with three 15 mL portions of hexane. After the removal of the last hexane wash, 25 mL of anhydrous THF was added and the flask thoroughly purged with dry N_2. A solution of 0.507 g (1.22 mmol) of the title tosylhydrazone **8** dissolved in 10 mL of THF was added to the sodium hydride suspension. Gas was evolved and a white ppt formed. This was stirred for 15 min at room temp. and then the salt was collected on a Hirsch funnel and dried in a vacuum desiccator overnight. This salt was placed in 30 mL of anhydrous THF in a pyrex flask to form a suspension and deoxygenated with bubbling N_2 for 30 min. To this suspension was added 0.022 mL (24.3 mg, 1.21 mmol, 1.0 equiv.) of 99.8% deuterium oxide. The suspension was irradiated with a 450 W Hanovia high pressure mercury lamp for 6 hr. The now yellow mixture was diluted with 150 mL of water and extracted twice with 200 mL of chloroform. The combined chloroform extracts were washed three times with 200 mL of water and dried over sodium sulfate. The chloroform was removed on the rotary evaporator and the residue analyzed by VPC (col B, 190°, 60 ml/min). An internal standard of 4,4′di-*tert*-butylbiphenyl was added and the yield of *o*-terphenyl **10** was determined to be 7.1%; an 11% yield of other VPC volatile products was found, in addition to a 13.3% yield of the 4,4-diphenyl-2,5-cyclohexadienone azine **13**. The *o*-terphenyl was collected by preparative VPC and subjected to 12.6 eV mass spectral analysis to determine deuterium incorporation if any. This was compared with undeuterated *o*-terphenyl. Undeuterated *o*-terphenyl gives *m/e* 230. The m + 1 peak (231) for 13 runs was 0.1956 ± 0.0076 of the m peak. For 11 runs of the experimental sample, m + 1 was 0.1940 ± 0.0068 of the m peak. This would give −0.0016 ± 0.0144 d_1 in the experimental sample or −0.16 ± 1% d_1 and thus, no detectable deuterium.

Preparation of 6-*bromo*-6-*deuterio*-4,4-*diphenylcyclohex*-2-*enone* **19**. A solution of 3.6380 g (11.1 mmol) of 6-bromo-4,4-diphenylcyclohex-2-enone **18**[5] was prepared in 14 mL of anhydrous THF in a 25 mL flask fitted with a magnetic stirrer and reflux condenser. The flask was thoroughly flushed with dry N_2 and 1.55 mL (77.5 mmol) of 99.8% D_2O was added. Then 3 mg of sodium was added and gas evolved as the sodium dissolved. After stirring at room temperature under nitrogen overnight, 15 mL of anhydrous benzene was added and the cloudy benzene solution dried over magnesium sulfate. The benzene was removed on the rotary evaporator to yield a brown oil whose NMR spectrum differed from that of 6-bromo-4,4-diphenylcyclohex-2-enone **18** in that the d of d at δ4.55 (C$\underline{H}$BrCO) was absent (greater than 90%) and the m at δ3.08 had collapsed to a simpler pattern. No attempt was made to purify this product. It was used as is in the preparation of 2-deuterio-4,4-diphenyl-2,5-cyclohexadienone **7a**.

Preparation of 2-*deuterio*-4,4-*diphenyl*-2,5-*cyclohexadienone* **7a**. The procedure of Zimmerman[5] used previously in the preparation of the undeuterated compound was followed. The crude 6-bromo-6-deuterio-4,4-diphenylcyclohex-2-enone **19** (assumed to be 11.1 mmol) was dehydrohalogenated using 2.79 g (37.8 mmol) of lithium carbonate and 3.19 g (36.7 mmol) of Li bromide. The crude product was recrystallized from ethanol to yield 1.486 g (6.02 mmol, 54%) of the deuterated dienone **7a**. The yield is calculated for the two steps from 6-bromo-4,4-diphenylcyclohex-2-enone **18**. Mass spectral analysis at 12.6 eV indicated the dienone to consist of 29.9 ± 1.2% d_0, 68.8 ± 1.7% d_1, and 1.3 ± 1.1% d_2. A second batch was run, which consisted of 53.7 ± 1.1% d_0, 43.3 ± 1.0% d_1, and 3.1 ± 0.1% d_2.

Preparation of 2-*deuterio*-4,4-*diphenyl*-2,5-*cyclohexadienone tosylhydrazone* **8a**. The same procedure used to prepare the undeuterated compound was followed. The reaction was carried out with 1.403 g (5.68 mmol) of the deuterated dienone and 1.062 g (5.70 mmol) of tosylhydrazine to yield 1.726 g (4.151 mmol, 73%) of the title tosylhydrazone **8a**.

Decomposition of the Li salt of 4,4-*diphenyl*-2,5-*cyclohexadienone tosylhydrazone* **8** *in diglyme and D oxide.* A 25 mL flask fitted with a magnetic stirrer, septum, reflux condenser, and gas inlet was charged with 0.643 g (1.55 mmol) of the title tosylhydrazone **8** dissolved in 6 mL of anhydrous diglyme. To this stirred solution at room temperature was added 0.88 mL (1.54 mmol) of 1.75 M MeLi in ether and then an additional 0.12 mL (0.21 mmol) of MeLi was added to induce formation of the deep gold color of the dianion. This solution was stirred at room temperature for 30 min and then 1.20 mL (1.20 g, 60.0 mmol) of 99.8% D oxide was added. The first drop caused the gold color to disappear. The septum was replaced with a stopper and this now cloudy solution was heated to reflux for 2 hr, during which time a yellow solid formed on the inside of the reaction flask. After cooling, the reaction was diluted with 75 mL of water and extracted with 40 mL of chloroform. The chloroform extract was washed with three 50 mL portions of water and dried over magnesium sulfate. The chloroform was removed on the rotary evaporator and the crude product purified by chromatography through a 0.5 × 10 in silica gel column eluting with dichloromethane. The chromatography was monitored by tlc (silica gel, dichloromethane). The fractions containing *o*-terphenyl were combined and the solvent removed on the rotary evaporator. An attempt was made to crystallize the resulting oil from methanol, but it was unsuccessful. The *o*-terphenyl was then isolated by preparative VPC (col A, 210°, 70 mL/min, 9.5 min). Mass spectral analysis at 16 eV indicated the *o*-terphenyl **10b** consisted of 2.48 ± 0.29% d_0, 98.07 ± 0.83% d_1, and −0.55 ± 0.71% d_2. The ^{13}C NMR spectrum of undeuterated *o*-terphenyl **10** was obtained (Fig. 1) and peaks assigned: ^{13}C NMR (20 MHz, $CDCl_3$), 141.48 ppm (C-1, C-1″), 140.53 (C-1′, C-2′), 130.56 (C-3′, C-6′), 129.84 (C-3, C-3″, C-5, C-5″), 127.82 (C-2, C-2″, C-6, C-6″), 127.43 (C-4′, C-5′), 126.39 (C-4, C-4″). The ^{13}C NMR spectrum of the experimentally derived 4-deuterio-*o*-terphenyl **10b** (Fig. 1) was assigned as follows: ^{13}C NMR (20 MHz, $CDCl_3$), 141.38 ppm (C-1, C-1″), 140.38 (C-1′, C-2′), 130.57 (C-6′), 130.47 (C-3′), 129.84 (C-3, C-3″, C-5, C-5″), 127.83 (C-2, C-2″, C-6, C-6″), 127.32 (C-5′), 126.39 (C-4, C-4″). Since essentially complete D incorporation was achieved, no signal for C-4′ (expected at 127.43) is observed.[9] Additionally, the signal for C-5′ is at 127.32, shifted 0.11 ppm upfield by the D isotope effect. The D isotope effect also explains the 0.10 ppm upfield shift of C-3′ from C-6′.

Decomposition of the Li salt of 2-*deuterio*-4,4-*diphenyl*-2,5-*cyclohexadienone tosylhydrazone* **8a** *in diglyme and water.* A 25 mL flask fitted with a magnetic stirrer, gas inlet, and septum was charged with 0.4059 g (0.975 mmol) of the title tosylhydrazone **8a** (29.9 ± 1.2% d_0, 68.8 ± 1.7% d_1, and 1.3 ± 1.1% d_2, determined from the ketone **7a**, dissolved in 5 mL of dry diglyme. The flask was thoroughly flushed with dry N_2 and 0.56 mL (0.98 mmol) of 1.75 M MeLi in ether was added. Then an additional 0.17 ml (0.30 mmol) of MeLi was added to induce the formation of the deep gold endpoint. This was stirred at room temp. for 45 min while the gold color faded. The 1.00 mL (55.6 mmol) of distilled water was added, which caused the solution to become cloudy. The septum was replaced with a reflux condenser and the solution was heated at reflux for 90 min under a N_2 atmosphere. After cooling, the reaction was diluted with 75 mL of water and extracted with 40 mL of benzene. The benzene extract was washed with six 75 mL portions of water to remove the diglyme and dried over magnesium sulfate. The benzene was removed on the rotary evaporator and the deuterated *o*-terphenyl was isolated by preparative VPC (col A, 210°, 75 ml/min, 9.5 min). Mass spectral analysis at 16 eV indicated that the *o*-terphenyl consisted of 27.8 ± 0.8% d_0, 72.6 ± 0.8% d_1, and −0.37 ± 0.34% d_2. The ^{13}C NMR spectrum of this mixture of undeuterated *o*-terphenyl **10** (27.4%), 3′-deuterio-*o*-terphenyl **10a** (36.3%), and 4′-deuterio-*o*-terphenyl **10b** (36.3%) was assigned as follows: ^{13}C NMR (20 MHz, $CDCl_3$), 130.53 ppm (C-3′ and C-6′ of **10**, C-6′ of **10a**, and C-6′ of **10b**, 130.41 (C-3′ of **10b**), 129.84 (C-3, C-3″, C-5, C-5″ of **10**, **10a**, and **10b**, 127.78 (C-2, C-2″, C-6, C-6″ of **10**, **10a**, and **10b**), 127.40 (C-4′ and C-5′ of **10**, and C-5′ of **10a**, 127.28 (C-4′ of **10a** and C-5′ of **10b**), 126.37 (C-4, C-4″ of **10**, **10a**, and **10b**).

Dry salt pyrolysis of the Li salt of 2-*deuterio*-4,4-*diphenyl*-2,5-*cyclohexadienone tosylhydrazone* **8a**. The procedure for the undeuterated case was followed, using 0.6415 g (1.544 mmol, 53.7 ± 1.1% d_0, 43.3 ± 1.0% d_1, and 3.1 ± 0.1% d_2, determined from the ketone **7a** of **8a** and titrating with 1.75 M methyllithium until the gold endpoint. The column chromatography yielded three main fractions, as before. The first column fraction was analyzed by VPC (col A, 210°, 60 mL/min) to give the following components and per cent compositions; biphenyl (32.3%), *o*-terphenyl (34.3%), compound C from the undeuterated case **12** (11.0%), *p*-terphenyl (10.2%), compound E (12.2%), and several other minor components. Anthracene was added as an internal standard and the yield of VPC volatile components was found to be 2.9%. The second column chromatography fraction yielded 0.2200 g (0.450 mmol, 58.3%) of azine **13**, while the third yielded 0.0789 g (22%) of high molecular weight residue. The *o*-terphenyl was isolated by preparative VPC and low voltage mass spectrometry showed that the product consisted of 58.18 ± 1.12% d_0, 41.32 ± 1.53% d_1, and 0.50 ± 0.50% d_2. The ^{13}C NMR spectrum was qualitatively very similar to the mixture of **10**, **10a**, and **10b** and was assigned in an identical manner: ^{13}C NMR (20 MHz, $CDCl_3$), 130.53 ppm (C-3′ and C-6′ of **10**, C-6′ of **10a**, and C-6′ of **10b**), 130.41 (C-3′ of **10b**), 129.84 (C-3, C-3″, C-5, C-5″ of **10**, **10a** and **10b**), 127.78 (C-2, C-2″, C-6, C-6″ of **10**, **10a**, and **10b**), 127.40 (C-4′ and C-5′ of **10**, and C-5′ of **10a**), 127.28 (C-4′ of **10a** and C-5′ of **10b**), 126.37 (C-4, C-4″ of **10**, **10a** and **10b**).

Incorporation of D on a C atom causes the loss of that ^{13}C NMR signal[9] and this decrease in signal intensity as compared to an undeuterated reference C atom can give the amount of D incorporation.[8] The double signal at 130.53–130.41 ppm was chosen to examine for D incorporation while the 126.37 signal was chosen to be the reference. These peaks were integrated by cutting and weighing to give means and standard deviations of 0.0245 ± 0.0004 g (eight samples) for the 130.53–130.41 peak and 0.0286 ± 0.0005 g (eight samples) for the 126.37 reference peak. In the region of 130.53–130.41, ^{13}C NMR signals for C-3′ and C-6′ of **10** and **10b** are present, but only the C-6′ signal is present for **10a**. This decrease in signal intensity was used to find the D incorporation in the following manner:

Let x = mole fraction of **10** (d_0), y = mole fraction of **10b** (d at C-4′), z = mole fraction of **10a** (d at C-3′) and c = detector response X moles of sample.

From the assignments of the signals at 130.53–130.41 and 126.37,

$$(2x + 2y + z)c = \text{area at } 130.53\text{–}130.41 = 0.0245$$
$$2(x + y + z)c = \text{area at } 126.37 = 0.0286.$$

These two equations may be combined to give

$$\frac{2x + 2y + z}{2x + 2y + 2z} = \frac{0.0245}{0.0286}.$$

It is also true that $x + y + z = 1$. From the mass spectral data, $x = 0.5818$ mole. The solution to the above equations is then $y = 0.1315$ mole and $z = 0.2867$ mole. The percentages of y and z are 31.4% y (**10a**) to 68.5% z (**10b**). The standard deviation is 8.8% using an error propagation formula.

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