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Carbanion Photochemistry. 11. 1,3-Diphenylisoindenylidene[1,2]

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Abstract: The irradiation of 2-chloro- or 2-bromo-1,3-diphenylindenyl anion (**5b** or **4b**) causes dehalogenation to yield a hypovalent intermediate best described as 1,3-diphenylisoindenylidene (**1**) or 1,3-diphenyl-1,2-dehydroindene (**20**). This intermediate undergoes facile CH insertion, addition to electron-rich olefins, and halide interchange.

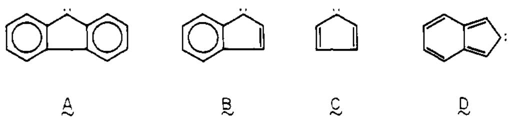
Hypovalent intermediates, including carbenes, provide entry into a rich variety of strained molecules with special reactivity. Carbenes themselves can exhibit a reactivity ranging from electrophilic to nucleophilic as a function of substituent.[3a] This ambiphilicity is associated, at least for singlet carbenes, with an sp^2-hybridized structure that places a pair of electrons in the lower energy sp^2 orbital and leaves the p orbital vacant. When the p orbital is part of a π-system that demands a pair of electrons to complete a Hückel array of orbitals, unconventional behavior may result. Such is apparently the case for fluorenylidene (A) and indenylidene (B)[3b] as well as the parent cyclopentadienylidene (C) and its derivatives. The case of isoindenylidene (D) should be particularly instructive, since the formal *o*-quinodimethane moiety disrupts the aromaticity of a second ring, and such an intermediate might be expected to have high electrophilicity. Recently we reported evidence for the generation of the first member of the class, 1,3-diphenylisoindenylidene (**1**).[1] Simultaneously, Jones and Pomfret reported preparation of 1,3-dimesitylisoindenylidene (**2**)[4a] using a more traditional diazo precursor. We now report further evidence of the nature of the highly reactive intermediate **1** and details of its unusual chemistry.

We have observed that, upon irradiation, a number of halogenated carbanions undergo facile loss of halide to yield hypovalent intermediates.[1,5] This is apparently a general phenomenon. Boule, Guyon, and Lemaire, for instance, have observed ring contraction products from irradiation of *o*-chlorophenolate anion,[6] and Seiler and Wirz reported the facile defluorination of trifluoromethyl phenolates.[7] Photodehalogenation of such carbanions offers the potential for facile generation of unconventional intermediates, and we undertook the study of the photochemistry of 2-haloindenyl anions as a possible route to the isoindenylidenes.

Results

Synthesis and Irradiation of 2-Bromoindenyl Anions. 2-Bromoindene (**3a**) and 2-bromo-1,3-diphenylindene (**4a**) were prepared by bromination/dehydrobromination of the corresponding indene. 2-Chloro-1,3-diphenylindene (**5a**) was prepared by thermolysis of 1,1-dichloro-2,2,3-triphenylcyclopropane using a modification of the procedure of Dehmlow and Schonefeld.[8] Their conjugate bases were prepared by deprotonation with potassium (methylsulfinyl)methide ("dimsyl") or potassium *tert*-butoxide in dimethyl sulfoxide, tetrahydrofuran, or *tert*-butyl alcohol. The solutions were allowed to equilibrate for 30 min, a trapping agent (if desired) was added in tenfold excess, and an aliquot was removed for analysis of any dark reaction. The solutions were then irradiated with a Hanovia 450-W medium-pressure mercury lamp using a 0.01 M $BiCl_3$ filter (which effectively excluded wavelengths below 355 nm) and monitored by gas chromatography to 60–90% conversion. The products were isolated by methylene chloride extraction and silica gel or alumina chromatography and then characterized by NMR, IR, and mass spectroscopy and, in the case of new compounds, elemental analysis. Finally, in cases of structural ambiguity, independent syntheses were carried out.

Chart I. Benzo-Fused Cyclopentadienylidenes



Our initial studies involved 2-bromoindenyl anion (**3b**). We were surprised to discover that this anion was photochemically inert, even in the presence of trapping agents. Thus our studies focused on the photochemistry of the diphenylindenyl anions **4b** and **5b**. Irradiation of either bromocarbanion **4b** or chloro carbanion **5b** led to rapid loss of halide and formation of the reduction product 1,3-diphenylindene (**6**) as well as a solvent incorporation product. The relative yields of the reduction and solvent addition products were a function of the solvent. With dimethyl sulfoxide as solvent, the reduction product **6** was produced in 20% yield and a new material was produced in 70% yield whose molecular formula $C_{23}H_{20}OS$ indicated the loss of halogen and incorporation of dimethyl sulfoxide. Gas chromatography and NMR spectroscopy indicated the presence of a 50:50 mixture of diastereomers. The presence of two AB quartets at δ 3.8 and 3.4 with a coupling constant of 14 Hz, together with characteristic singlets at δ 2.50 and 2.25 suggested the presence of the (methylsulfinyl)methyl group and indicated that the unknown product was 1-((methylsulfinyl)methyl)-1,3-diphenylindene (**7**, see Figure 1). The photochemistry of either chloro or bromo anion was identical in product composition. However, the bromo anion required 4–6 times longer irradiation time for similar conversions.

The structure of **7** was confirmed by independent synthesis (see Figure 2). Thus 1,3-diphenylindenyl anion was treated with chloromethyl thioether to yield 1-((methylthio)methyl)-1,3-diphenylindene (**8**) in 54% yield along with the product of a novel addition–elimination, 1,4-diphenylnaphthalene, in 39% yield. Oxidation of thioether **8** with hydrogen peroxide led to formation of sulfoxide **7** which was in all respects identical with the photochemical product with one exception: the diastereomeric ratio was 60:40.

When the irradiation was carried out in *tert*-butyl alcohol as solvent, in addition to reduction product **6**, two new products were formed. The first was identified as 1-*tert*-butoxy-1,3-diphenylindene (**9**) on the basis of mass and NMR spectroscopy as well

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[1] (a) A preliminary communication of this work has appeared.[1b] (b) Tolbert, L. M.; Siddiqui, S. *J. Am. Chem. Soc.* **1982**, *104*, 4273.

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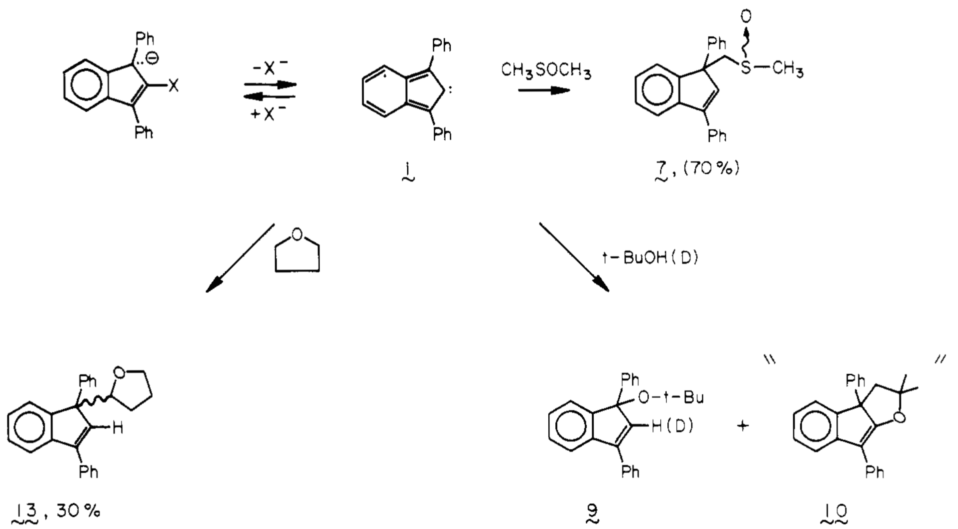

Figure 1. Solvent incorporation products.

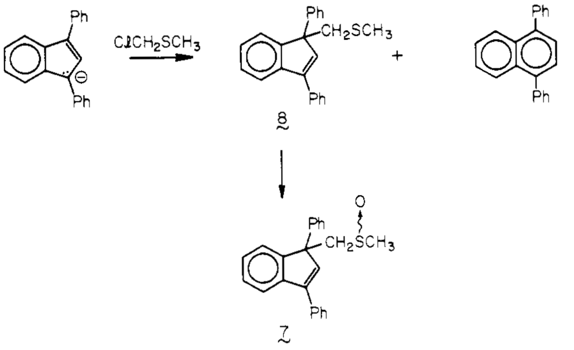

Figure 2. Synthesis of Me_2SO adduct.

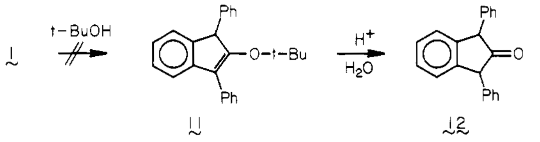

Figure 3.

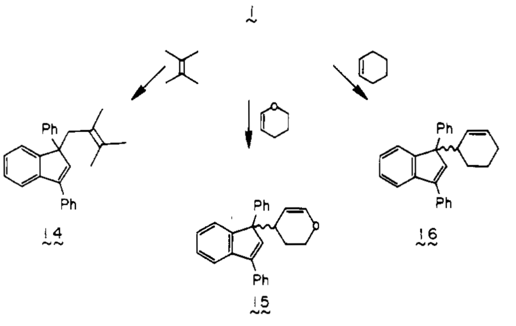

Figure 4. Products with allylic olefins.

and the molecular ion in the mass spectrum showed the incorporation of a single deuterium (see Figure 1). Neither 1,3-diphenylindene nor adduct **10**, however, indicated deuterium incorporation.

The products from irradiation of chloroindenyl anion **5b** in tetrahydrofuran consisted of 1,3-diphenylindene (8%) and a product (30%) that we had earlier observed upon irradiation of 1,3-diphenylindenyl in tetrahydrofuran under $S_{RN}1$ conditions and had assigned as a solvent adduct.[2b] On the basis of the mass spectrum and NMR spectrum, which indicated half integral styryl resonances at δ 6.5 and 6.7, as well as multiplets at δ 4.75–5.05 (1 H) and δ 3.70–3.85 (2 H), the solvent adduct was assigned the as its ready conversion in dilute hydrochloric acid to 1-chloro-1,3-diphenylindene. The second new product was tentatively assigned structure **10** on the basis of a one proton doublet at δ 2.75–2.90 (J = 13 Hz) and a one proton doublet at δ 2.00–2.15 (J = 13 Hz), as well as inequivalent methyl groups at δ 1.45 and 1.20 (see Figure 1). Both the filter solution employed and the red-orange color of the solution ensured that only the anion was irradiated.

No evidence was obtained for the product of reversed solvent addition **11**. A typical reaction mixture subjected to aqueous acid hydrolysis failed to yield detectible amounts of the expected acid hydrolysis product of **11**, 1,3-diphenyl-2-indanone (**12**), which had been prepared independently (see Figure 3). When the irradiation was repeated with *tert*-butyl alcohol-d_1, *tert*-butyl ether **9** was produced in which the vinyl resonance at δ 6.6 had disappeared structure 1-(2-tetrahydrofuryl)-1,3-diphenylindene (**13**) as a mixture of diastereomers.

Irradiation in the Presence of Trapping Agents. The irradiation of **4b** and **5b** in the presence of olefins containing abstractable protons has been reported.[1b] Thus added 2,3-dimethylbutene produces indene **6** in 10% yield as well as 1-(2,3-dimethylbut-2-enyl)-1,3-diphenylindene (**14**) in 60% yield. Added dihydropyran produced indene **6** (22%) and 1-(4-oxacyclohex-2-enyl)-1,3-diphenylindene (**15**, 50%), the latter as a 50:50 mixture of diastereomers, while added cyclohexene produced indene **6** (30%) and 1-cyclohex-2-enyl-1,3-diphenylindene (**16**) as a mixture of diastereomers in ca. 60% yield (see Figure 4).[1b]

With electron-rich olefins not bearing abstractable protons, addition products were observed (see Figure 5). Ethyl vinyl ether produced 9-phenyl-3,4-benzfluorene (**17**) in 50% yield and 5% of the reduction product **6**. Irradiation of **5b** with 1,1-dimethoxyethylene produced indene (**6**, 15%) and two new products in 18% and 30% yield by gas chromatographic analysis. Upon workup, the 18% yield product had disappeared, while the 30% yield product has increased to 46% of the reaction mixture. The latter product, upon purification, exhibited characteristic peri protons at δ 8.8 and 8.4 in the NMR and a one-proton singlet at δ 6.8. The latter chemical shift is typical of a α-proton on an α-methoxynaphthalene. On the basis of this spectral information and an exact mass of m/e 322.124, this unknown adduct was assigned the structure 2-methoxy-9-phenyl-3,4-benzfluorene (**18**).

Irradiation of **5b** in dimethyl sulfoxide with added 2,3-dimethyl-1,3-butadiene produced, in addition to indene **6** (10%) a new product in 60% yield. This product had exact mass of m/e 348.188 (calcd for $C_{27}H_{24}$ m/e 348.188), again indicating loss of chloride and addition of olefin. The molecular ion at m/e 348 (100%), indicated a condensed polycyclic structure, and the proton NMR indicated the absence of styryl protons. Two allylic methyl singlets (δ 1.60, 1.48) and two allylic AB quartets (doublets centered at δ 2.09, 2.64, 2.96, and 3.14) indicated the unknown

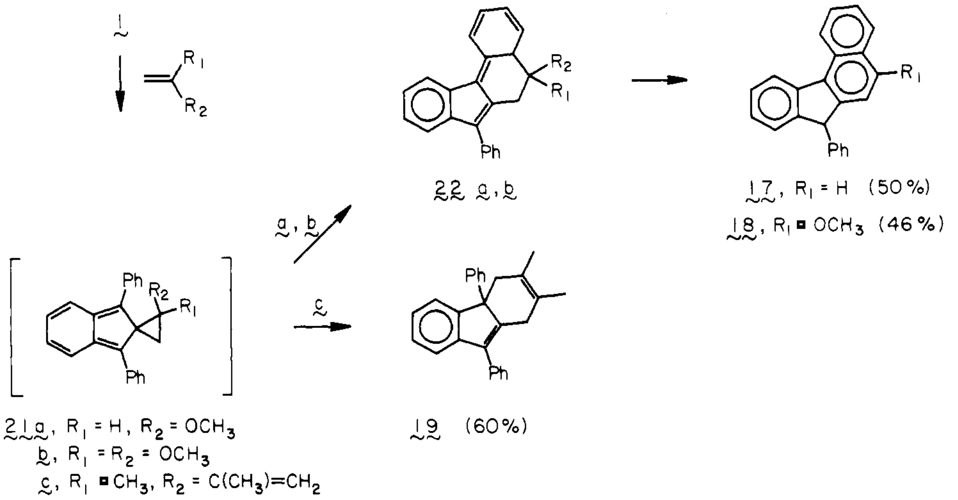

Figure 5. Adducts with electron-rich olefins.

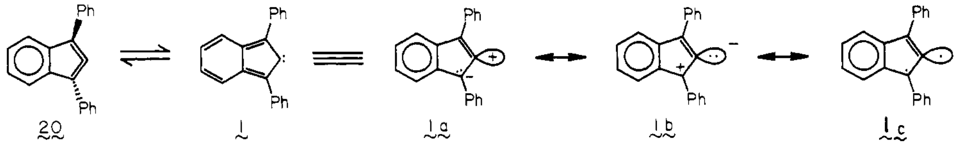

Figure 6. Carbene vs. twisted allene structure.

was 2,3-dimethyl-4a,9-diphenyl-1,1a,4,4a-tetrahydrofluorene (**19**).

In contrast to these results, irradiation of chloroanion **5b** in the presence of the electron-deficient olefin dimethyl fumarate gave, after 4 h, a 50% yield of reduction product 1,3-diphenylindene (**4**) and no evidence of addition to the fumarate moiety.

Finally, irradiation of chloro anion **5b** in dimethyl sulfoxide with added benzene, after 90% conversion and isolation of products, gave 1,3-diphenylindene (**6**, 22%), 1,1,3-triphenylindene (5%), biphenyl (5%), and the apparent dimer of 1,3-diphenylindenyl radical (30%).

Photopromoted Halogen Interchange. Since certain carbenes undergo addition of halogen nucleophiles, the photochemistry of both bromo anion **4b** and chloro anion **5b** in the presence of added halide anion was examined. Irradiation of bromoanion **4b** in the presence of a fivefold equivalent of potassium chloride produced, in addition to a 10% yield of 1-((methylsulfinyl)methyl)-1,3-diphenylindene (**7**), a 15% yield of 2-chloro-1,3-diphenylindene (**5a**). Conversely, irradiation of chloroindenyl anion **5b** with a fivefold equivalent of potassium bromide gave, in addition to 45% of solvent adduct **7**, a 1% yield of 2-bromo-1,3-diphenylindene (**4a**).

The role of halide quenching (or facilitation) in the photochemistry of the haloindenyl anions **4b** and **5b** was investigated by means of a relative quantum yield experiment using a merry-go-round apparatus. Thus solutions of each anion at identical concentrations were irradiated in the presence of excess potassium halide. The formation of dimethyl sulfoxide adduct was **7** served as the reference reaction, and the uncorrected yields of the adduct as a function of added halide are reported in Table I. The results are summarized as follows: added halide, either chloride or bromide, quenched the photochemistry of the chloroindenyl anion but facilitated the photochemistry of the bromoindenyl anion. These results are discussed below.

Discussion

The Nature of the Reactive Intermediate. The facile halogen interchange observed in the photochemistry of **4b** and **5b** requires an intermediate that can reversibly add nucleophiles. By analogy with the known propensity of carbenes to add halide ions, 1,3-diphenylisoindenylidene (**1**) appears to be a likely candidate. However, the alternate hypovalent intermediate 1,3-diphenyl-1,2-didehydroindene (**20**) is also possible (see Figure 6). The stability of the anion **4b** or **5b** resulting upon halide addition together with the strain associated with a 5-membered ring allene may make this a feasible reaction pathway. Moreover, Diels–Alder cycloadditions provide attractive mechanistic routes to carbocyclic molecules **17**–**19** if allene **20** is involved. In general, however, the electrophilicity of the intermediate and its propensity for hydrogen atom abstraction are analogous to the properties of other electron-deficient carbenes.[9]

Table I. Effect of Added Halide on Yield of Me_2SO Adduct **7**

substituent[a]	halide[b]	yield, %
Cl		53
Cl	Cl^-	30
Cl	Br^-	23
Br		1–2
Br	Cl^-	7–8
H		0

[a] Anion at 1.25×10^{-2} M. [b] Halide at 6.0×10^{-2} M as potassium salt.

The singlet ground state of **1** may be thought of as a linear combination of two zwitterionic states **1a** and **1b** as well as diradical state **1c**. The properties of this carbene will depend upon the relative importance of each valence bond contributor. We can relate the electronic demand for the valence bond structure **1a** containing six electrons in the π-system (**1a**) to the stability of the corresponding carbanion as measured by pK_a. In dimethyl sulfoxide, the pK_a's of cyclopentadiene, 1,3-diphenylcyclopentadiene, fluorene, and 1,3-diphenylindene are 18,[10] 14,[11] 23,[12] and 13,[13] respectively, indicating greatest stabilization for delocalization of electrons in the π-system of **1**. Moreover, the reference carbon acid for **1** should be the even more acidic 1,3-diphenylisoindene, which should compensate for any stabilization by the benzo group for valence bond structure **1b**. Also, NMR data and Hückel calculations for the diazo precursor to dimesitylisoindenylidene **2** indicate greater delocalization in the isoindenylidene structure,[4] in contrast to cyclopentadienylidene or

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indenylidene. Thus of cyclopentadienylidene, 2,5-diphenylcyclopentadienylidene, fluorenylidene, and **1**, we might predict the greatest electrophilicity for the latter. In fact, the ready addition of electron-rich, as opposed to electron-poor, olefins to **1** is in accord with this analysis. The propensity of **1** to undergo C–H insertion reactions is also reminiscent of the behavior of cyclopentadienylidene. Admittedly, cyclopentadienylidene also gives cyclopropanation products with simple olefins, products which we failed to observe with **1**, although a cyclopropane intermediate can be invoked in the formation of cycloadducts **17–19**. For these cases, the instability associated with the spirocyclopropa[isoindene] ring system may result in ready rearrangement to yield the observed products. In the particular case of 1,1-dimethoxyethylene, the presence of an unstable precursor to **18** with GC retention time consistent with a precursor containing both methoxy moieties could be explained by either cyclopropane **21b** or dihydrobenzfluorene **22b**.

Mechanism of C–H Insertion. The products of C–H insertion **7**, **13**, **14**, **15**, and **16** clearly involve hydrogen atom abstraction followed by radical–radical recombination. First, allylic rearrangement is observed in the case of adduct **15**, although a mechanism involving an ene reaction followed by a Cope rearrangement is a plausible, if unlikely, possibility. Second, when products are diastereomeric, i.e., **7**, **13**, **15**, and **16**, these are produced in a statistically random 50:50 ratio, in contrast to the ratios from direct synthesis. Third, in the case of irradiation in *tert*-butyl alcohol d_1, the reduction product **6** does not incorporate deuterium, indicating the formation of the 1,3-diphenylindenyl radical through hydrogen atom abstraction. Finally, irradiation of **5b** in the presence of benzene led to the formation of biphenyl, implicating the presence of phenyl radical. The presence of such hydrogen atom abstraction products has been associated with the intervention of triplet carbenes,[14] although evidence is accumulating that for electron-deficient carbenes such as fluorenylidene the triplet and singlet states may be in rapid equilibrium.[14]

The Mechanism of O–H Insertion. The products of addition of *tert*-butyl alcohol are observed only when alcohol is solvent, despite the use of identical *tert*-butoxide concentrations in dimethyl sulfoxide as solvent. This fact coupled with the exclusive deuterium incorporation at C-2 in deuterated *tert*-butyl alcohol, indicates that protonation at C-2 precedes or is synchronous with nucleophilic addition of alcohol. This is in marked contrast to the chemistry of cyclopentadienylidene, for which formation of the C–O bond precedes proton incorporation.[15] The reasons for this divergence are obscure. Steric hindrance may simply prohibit formation of **11** via the nucleophilic pathway that occurs readily for chloride and bromide. Alternatively, formation of **11** may be photochemically reversible. More puzzling is the formation of a product of formal addition/oxidation represented by the tentative structure **12**. We offer no plausible mechanism.

Relative Efficiency of Dehalogenation. The greater efficiency for chloride as opposed to bromide loss upon photoexcitation is in contrast to the typical nucleofugic order. This probably reflects not a greater rate of bromide loss in the primary process but efficient quenching of the photochemistry by bromide return. That halide return can act as a quenching process is indicated by the quenching of chloro anion photochemistry in the presence of added halide. Chloride facilitates the photodehalogenation of bromo anion **4b**, presumably by capturing the intermediate carbene and then undergoing expulsion in a second photochemical step. For this to make kinetic sense, the major deactivation pathway must involve return of bromide within the cage. The appearance of halide exchange products is strong evidence that the efficiency of the reaction is controlled by the rate of halide return.

Implications for the Chemistry of Allenes. Recent studies on allene photochemistry have focused on the possibility of "sudden polarization" as a mechanism for excited-state decay.[16] Thus the excited state of diphenylallene can undergo demotion to a zwitterionic state that is captured by nucleophilic solvent. The planar zwitterionic state may thus be thought of as an excited state of the twisted allene. The zwitterionic valence bond structures **1a** and **1b** may be considered as benzo-bridged analogues of the diphenylallene polarized state, and the question of **20** vs. **1** as the correct structure of our intermediate reduces to that of determining whether such cyclization reverses the order of the ground and excited states for such allenes. This question can be answered more appropriately by allenes constrained in a small ring. The analogous photochemical synthesis of such strained allenes we are now exploring.

Experimental Section

Materials. 2-Bromoindene (3a) was synthesized in 20% yield by the method of Porter and Suter.[17] The solid product was recrystallized from methanol to yield colorless prisms: mp 38–39 °C (lit.[17] mp 38–39 °C); NMR (CCl_4) δ 7.0–7.4 (4 H, m), 6.8 (1 H, s), 3.4 (2 H, s).

2-Bromo-1,3-diphenylindene (**4a**) was synthesized in 50% yield by the method of Koelsch without modification.[18] The colorless prisms had a melting point of 68–69 °C (lit.[18] mp 66–68 °C): NMR ($CDCl_3$) δ 7.05–7.67 (14 H, m), 4.65 (1 H, s); MS, *m/e* 348 (parent), 346, 267, 265.

2-Chloro-1,3-diphenylindene (**5a**) was synthesized by a modification of the method of Dehmlow and Schonefeld,[8] which involved preparation and thermolysis of 1,1-dichloro-2,2,3-triphenylcyclopropane.

1,1-Dimethoxyethylene was synthesized in two steps using a slight modification of the literature procedure.[19]

1,1-Dichloro-2,2,3-triphenylcyclopropane. An aqueous solution of 120 g of 50% sodium hydroxide was added dropwise to a chilled flask containing 9.6 g (37.5 mmol) of triphenylethylene, 150 g of ethanol-free chloroform, and 750 mg of triethylbenzylammonium chloride. The ice bath was maintained during addition, and the reaction mixture was stirred vigorously for 65 h at room temperature. Cold water was added, and the brown residue was removed by filtration. The organic layer was separated and the aqueous layer extracted twice with chloroform. The combined chloroform extracts were dried over anhydrous $MgSO_4$. Solvent removal in vacuo yielded 8.0 g of a brown glass, which when scratched in petroleum ether (bp 35–60 °C) at dry ice–acetone temperature produced crystals. The product was recrystallized from petroleum ether (bp 35–60 °C) to yield 7.2 g (58%) of fluorescent colorless crystals: mp 105–107 °C (lit.[8] mp 107 °C); NMR ($CDCl_3$) δ 6.9–7.4 (15 H, m), 3.55 (1 H, s).

A 7.35-g (21.6-mmol) portion of 1,1-dichloro-2,2,3-triphenylcyclopropane was placed in a large sublimator and sublimed at 150–170 °C at 10^{-2} torr. Hydrogen chloride generated from the reaction was trapped with a solid KOH trap placed between the sublimator and the vacuum line. The 6.41 g of brown product was purified by silica gel column chromatography (hexane eluent) to yield 6.09 g (93%) of pure 2-chloro-1,3-diphenylindene as a colorless oil which crystallized from petroleum ether maintained in a dry ice–acetone bath. Recrystallization from petroleum ether (bp 35–60 °C) gave 4.70 g of white crystalline product: mp 65–66 °C (lit.[8] mp 64.5 °C); NMR ($CDCl_3$) δ 7.0–7.77 (14 H, m), 4.55 (1 H, s); MS, *m/e* 304, 302, 267.

1-((Methylthio)methyl)-1,3-diphenylindene. 1,3-Diphenylindenyl anion was prepared by treating 99 mg (0.37 mmol) of 1,3-diphenylindene with 89 mg (0.8 mmol) of potassium *tert*-butoxide in 7 mL of dry tetrahydrofuran under argon. An 81-mg (70-μL, 0.84-mmol) portion of chloromethyl methyl sulfide (Aldrich) was added to the anion at 0 °C with vigorous stirring. The reaction mixture was stirred at room temperature for 1 h and quenched with water. The crude residue obtained after methylene chloride extraction chromatographed on a 2.5 × 8.0 cm column in silica gel (100 mL) yielded 40 mg of 1,4-diphenylnaphthalene as colorless needles, mp 130–131 °C (lit.[20] mp 134–135 °C). A second fraction yielded pale yellow crystals of the desired product: 66 mg (54%); mp 64–68 °C; NMR ($CDCl_3$) δ 7.06–7.64 (14 H, m), 6.64 (1 H, s), 3.52 (1 H, d, J = 13 Hz), 3.10 (1 H, d, J = 13 Hz), 1.93 (3 H, s); MS, *m/e* 328 (100), 281, 267, 203, 182.

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1-((Methylsulfinyl)methyl)-1,3-diphenylindene.[22] To a solution of 50.4 mg (0.153 mmol) of 1-((methylthio)methyl)-1,3-diphenylindene in 100 mg (126 μL) acetone was added 16 μL (0.154 mmol) of 30% hydrogen peroxide. The mixture was stirred for 36 h and then worked up by solvent removal and preparative thin-layer chromatography to yield 50 mg (94%) of a colorless solid. Gas chromatographic analysis showed two components in a ratio of 3:2. This was purified by preparative thin-layer silica gel chromatography and eluted with chloroform/hexane (4:1): NMR ($CDCl_3$) δ 7.2–7.6 (14 H, m, arom), 6.85 (0.5 H, s, isomer A, styryl), 6.74 (0.5 H, s, isomer B, styryl), 3.73–3.90 (1 H, AB q, *J* = 14 Hz, isomer A, CH_2SO), 3.33–3.48 (1 H, AB q, *J* = 14 Hz, CH_2SO), 2.52 and 2.28 (3 H, 2 s); MS, *m/e* 344, 328, 281, 267, 204, 203.

1-Cyclohex-2-enyl-1,3-diphenylindene. To a solution of 1,3-diphenylindenyl anion generated from 72 mg (0.26 mmol) of the hydrocarbon and 88 mg (0.8 mmol) of potassium *tert*-butoxide in 8 mL of tetrahydrofuran was added 100 mg (0.86 mmol) of 3-chlorocyclohexene (Pfaltz and Bauer) in 1 mL of tetrahydrofuran at 0 °C. The solution was stirred at 0 °C for 30 min and then at room temperature for 30 min. Water was added, the mixture was extracted with ether, and the dried extract was purified by silica gel thin-layer chromatography using hexane as solvent. The yield was 54 mg (60%) of the cyclohexenylindene as a colorless oil: NMR ($CDCl_3$) δ 7.1–7.7 (14 H, M, arom), 6.61 (1 H, two overlapping s, styryl), 5.68 (1 H, s, isomer A, vinyl), 5.46–5.65 (0.5 H, d, *J* = 10 Hz, isomer B, vinyl), 5.05–5.3 (0.5 H, d, *J* = 10 Hz, isomer B), 3.2–3.5 (1 H, m), 1.4–2.0 (6 H, m, methylene); MS *m/e* 267 (100), 265, 91, 84, 81. Anal. Calcd for $C_{27}H_{24}$: C, 93.05; H, 6.94. Found: C, 92.85; H, 7.10.

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in Me_2SO. A 181.4-mg (0.6-mmol) portion of 2-chloro-1,3-diphenylindene was placed in a 35-mL photolyzing tube, degassed several times, and finally maintained under an argon atmosphere. Distilled Me_2SO (19 mL) was added and the solution degassed once more. A 6-mL Me_2SO solution of 0.11 M (0.66 mmol) of potassium *tert*-butoxide was introduced under argon. The solution was allowed to equilibrate for 30 min and the reaction irradiated for 2 h at room temperature. Gas chromatographic analysis of a quenched aliquot (0.5 mL) showed 90% disappearance of starting indene. The reaction mixture was quenched with water (10 mL). The solution was filtered to remove a precipitate, the aqueous mixture was extracted several times with dichloromethane, and the combined dichloromethane extracts were washed three times with brine. Drying of the organic phase over anhydrous $MgSO_4$ and concentration in vacuo yielded 117 mg of a crude mixture, which was subjected to preparative silica gel thin-layer chromatography and eluted with chloroform/hexane (9:1). The fractions were collected: F-1, 15 mg (9%) of 1,3-diphenylindene; F-2, 60 mg (30%) of 1-((methylsulfinyl)methyl)-1,3-diphenylindene as a 50:50 mixture of diastereomers by gas chromatography.

Irradiation of 2-Bromo-1,3-diphenylindenyl Anion in Me_2SO. When an analogous reaction to that described above was carried out with 2-bromo-1,3-diphenylindenyl anion in Me_2SO and monitored by gas chromatography, slow formation of 1-((methylsulfinyl)methyl)-1,3-diphenylindene in the same ratio (1:1) was observed. A typical reaction time employing this substrate was 6–7 h for comparable conversion (approximately 90%) as opposed to 2 h using 2-chloro-1,3-diphenylindenyl anion.

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in Cyclohexene/Me_2SO. 2-Chloro-1,3-diphenylindenyl anion was generated from 303.3 mg (1.00 mmol) of the hydrocarbon, 1.1 mmol of potassium *tert*-butoxide in Me_2SO, and 5 mL of Me_2SO was degassed several times and maintained under argon. Cyclohexene (10–12 mL deoxygenated by purging with argon) was added. The two-phase mixture thus formed was irradiated for 2.5 h and the reaction quenched with water. Gas chromatographic analysis indicated 30% 1,3-diphenylindene and 66% other products. Methylene chloride extraction yielded 330 mg of brown residue, which was purified by silica gel column chromatography, eluting with hexane. A fraction containing 240 mg of a colorless glassy solid proved to be 1-cyclohex-2-enyl-1,3-diphenylindene (45% yield) slightly contaminated by 1,3-diphenylindene.

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in Dihydropyran/Me_2SO. To the anion made from 303 mg (1.00 mmol) of 2-chloro-1,3-diphenylindene, 5 mL of Me_2SO, and a 5-mL Me_2SO solution of 0.21 M potassium *tert*-butoxide was added 20 mL of deoxygenated dihydropyran under argon. The reaction mixture was irradiated for 2.5 h at room temperature and then quenched with water. The residue obtained after methylene chloride extraction showed 45% of an adduct, 20% of 1,3-diphenylindene, and 10% starting material by gas chromatography. The residue was purified by silica gel column chromatography. Fraction 1 (500 mL of hexane) gave 21.3 mg (8%) of 1,3-diphenylindene. Fraction 2 (250 mL of hexane) consisted of starting 2-chloro-1,3-diphenylindene (20 mg, 8–9%). Fraction 3 (9:1 hexane/ether, 500 mL) yielded 66 mg of an unknown material. Fraction 4 (9:1 hexane/ether, 250 mL) was 50 mg (15%) of 1-(4-oxacyclohex-2-enyl)-1,3-diphenylindene: NMR ($CDCl_3$) δ 7.15–7.8 (14 H, m, arom), 6.86 (0.5 H, s, isomer A, styryl), 6.52 (0.5 H, s, isomer B, styryl), 5.4–5.8 (1 H, m, isomer A, vinyl), 4.9–5.3 (1 H, m, isomer B, vinyl), 3.6–4.2 (3 H, m, CH_2 and methine), 1.8–2.5 (2 H, m, methylene); MS, *m/e* 350, 267, 83; calcd for $C_{26}H_{22}O$ 350.167, found 350.165.

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in 2,3-Dimethyl-2-butene/Me_2SO. To 31 mg (0.1 mmol) of 2-chloro-1,3-diphenylindene in a 10-mL irradiation tube was added 1 mL of 0.11 M potassium *tert*-butoxide in Me_2SO. A deoxygenated sample (10–15 mL) of 2,3-dimethyl-2-butene was added under argon and the reaction mixture irradiated for 90 min using 0.1 M $BiCl_3$ filter. The residue (28 mg) obtained after quenching and the extraction was purified by preparative thin-layer chromatography (silica gel) to yield 11 mg (30%) of 1-(2,3-dimethylbut-2-enyl)-1,3-diphenylindene: NMR ($CDCl_3$) δ 7.1–7.7 (14 H, m, arom), 6.62 (1 H, s, styryl), 3.18–3.33 (1 H, d, *J* = 13 Hz, methylene), 2.85–3.0 (1 H, d, *J* = 13 Hz, methylene), 1.50 (6 H, s), 1.19 (3 H, s, CH_3); MS, *m/e* 350 (parent), 267, 265, 190, 83; calcd for $C_{27}H_{26}$ 350.203, found 350.191.

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in the Presence of Ethyl Vinyl Ether/Me_2SO. To the anion made from 303.6 mg (1 mmol) of 2-chloro-1,3-diphenylindene, a 5-mL Me_2SO solution of 0.215 M potassium *tert*-butoxide, and 2 mL of Me_2SO was added 25 mL of freshly distilled ethyl vinyl ether. The mixture was irradiated for 3 h. The mixture was quenched with 10 mL of water. Analysis of the methylene chloride extract indicated the presence of 50% of 9-phenyl-3,4-benzfluorene together with 5% of 1,3-diphenylindene. The mixture was applied to a 50-cm column of silica gel and eluted with hexane. Fraction 1 (500 mL) gave 20 mg (7%) of 1,3-diphenylindene. Fraction 2 (500 mL) yielded 62 mg of pure 9-phenyl-3,4-benzfluorene crystallized on standing. Recrystallization from ethanol yielded colorless crystals, mp 137–138 °C (lit.[21] mp 138 °C). Fraction 3 (500 mL) yield an additional 40 mg of the adduct. The total isolated yield was 35%: NMR ($CDCl_3$) δ 8.73 (1 H, d, *J* = 8 Hz), 8.32 (1 H, d, *J* = 8 Hz), 8.0–7.0 (13 H, m), 5.06 (1 H, s, benzhydryl); ^{13}C NMR ($CDCl_3$) 54.91, 122.88, 123.28, 123.92, 125.29, 126.67, 126.93, 127.43, 128.31, 128.49, 128.73, 129.25, 129.47, 133.72, 141.05, 142.04, 146.83, 149.15 ppm; MS, *m/e* 292 (parent), 215 (M − 77); calcd for $C_{23}H_{16}$ 292.125, found 292.124.

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in *tert*-Butyl Alcohol. The chloroindene (520 mg, 1.7 mmol) was dissolved in 50 mL of oxygen-free *tert*-butyl alcohol (deoxygenated by the freeze–pump–thaw method) under argon. A 10-mL *tert*-butyl alcohol solution of 0.2 M potassium *tert*-butoxide was added. The reaction mixture was irradiated for 2 h upon which a brown precipitate formed. The reaction was quenched with water and the solvent removed by distillation. The reaction mixture was extracted with ether, and the organic extracts were dried over anhydrous potassium carbonate. The extract was purified by alumina column chromatography eluting with hexane. Fraction 1 (250 mL) yielded 5% of 1,3-diphenylindene. Fraction 2 (650 mL) yielded 103 mg (isolated 20% yield) of a colorless oil which crystallized from hexane in a dry ice–acetone bath to yield colorless crystals, mp 85–88 °C, of 1-*tert*-butoxy-1,3-diphenylindene (**9**): NMR ($CDCl_3$) δ 7.2–7.8 (14 H, m, arom), 6.6 (1 H, s, styryl), 1.12 (9 H, s, $(CH_3)_3CO$); MS, *m/e* 340, 284 (100). Anal. Calcd for $C_{25}H_{24}O$: C, 88.19; H, 7.10. Found: C, 87.79; H, 6.95. Fraction 3 (150 mL) yielded 19 mg (3.5%) of a light yellow oil: NMR ($CDCl_3$) δ 7.15–7.8 (14 H, m, arom), 2.75–2.9 (1 H, d, *J* = 13 Hz, methylene), 2.0–2.15 (1 H, d, *J* = 12 Hz, methylene), 1.45 (3 H, s, CH_3), 1.2 (3 H, s, CH_3); MS, *m/e* 338 (parent), 285, 282. The residue from the column after methanol extraction consisted of a mixture of generally unknown composition, although one product was identified as 1,3-diphenyl-1-indenol (20%).

Hydrolysis of 1-*tert*-Butoxy-1,3-diphenylindene (9). To a 20-mg (0.06-mmol) portion of 1-*tert*-butoxy-1,3-diphenylindene was added a 2-mL portion of 50% hydrochloric acid, and the flask was warmed on a steam bath for 5 min. Ether extraction, drying, and solvent removal in vacuo yielded 1-chloro-1,3-diphenylindene: NMR ($CDCl_3$) δ 7.0–7.6 (14 H, m), 6.7 (1 H, s); MS, *m/e* 304, 302, 267.

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in *tert*-Butyl Alcohol-*d*. The same above procedure was repeated with 200 mg (0.66 mmol) of 2-chloro-1,3-diphenylindene, 15 mL of *tert*-butyl alcohol-*d*, and a 10-mL *tert*-butyl alcohol-*d* solution of 78 mg (0.7 mmol of potassium *tert*-butoxide. The reaction mixture was quenched with water (H_2O) after 2 h of irradiation. Alumina column chromatography of the residue using hexane as eluent yielded 1,3-diphenylindene (MS, *m/e* 338, 285, 282) followed by 69.1 mg (35%) of 1-*tert*-butoxy-1,3-diphenyl-2-

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[22] This sulfoxide yielded elemental analyses within 1% of the calculated value which could not be improved by further chromatography, presumably because of the presence of some overoxidized contaminant. The molecular ion was insufficiently strong for unambiguous assignment of exact mass.

deuterioindene: mp (**9**, 2-D) 88–91 °C; NMR ($CDCl_3$) δ 7.2–7.8 (14 H, m), 1.25 (9 H, s, $(CH_3)_3CO$); MS, *m/e* 341 (parent, 5), 340, 285 (M − 56, 100), 268. A second fraction isolated by column chromatography yielded 25 mg of a oil with spectra in all respects identical with those for fraction 3 above: MS, *m/e* 338, 285, 282.

Irradiation of 2-Bromo-1,3-diphenylindenyl Anion in the Presence of Potassium Chloride in Me_2SO. To the anion derived from 30.2 mg (0.1 mmol) of 2-bromo-1,3-diphenylindene and an equivalent of potassium *tert*-butoxide in 1 mL of Me_2SO was added 7 mL of a Me_2SO solution containing 36 mg (0.48 mmol) of potassium chloride. The mixture was irradiated for 1 h and quenched. The residue obtained after workup was analyzed by gas chromatography. It indicated formation of 2-chloro-1,3-diphenylindene in 15% yield in addition to 1-((methylsulfinyl)methyl)-1,3-diphenylindene in 10% yield. Mass spectrum of the residue: *m/e* 348, 344, 328, 302, 281, 267.

In a similar reaction, irradiation of 2-chloro-1,3-diphenylindenyl anion in the presence of bromide ion showed the presence of 2-bromo-1,3-diphenylindene (1% by GC).

Irradiation of 2-Halo-1,3-diphenylindenyl Anion in the Presence of Halide Ions in Me_2SO. Six 15-mL irradiation tubes (marked 1, 2, 3, 4, 5, and 6) were used. To each of tubes 1, 2, and 3 was introduced 15.12 mg (0.05 mmol) of 2-chloro-1,3-diphenylindene. To each of tubes 4 and 5 was introduced 17.4 mg (0.05 mmol) of 2-bromo-1,3-diphenylindene. Tube 6 contained 13.4 mg (0.05 mmol) of 1,3-diphenylindene. The tubes were degassed and kept under argon. A 1-mL freshly prepared Me_2SO solution of 0.055 M potassium *tert*-butoxide was introduced into each tube to generate the respective anions. Dimethyl sulfoxide (3 mL) was added to each of the tubes 1, 4, and 6. A 3-mL Me_2SO solution of 0.08 M potassium chloride (i.e., 0.24 mmol of KCl) was added to tubes 2 and 5. To tube 3 was added a 3-mL Me_2SO solution of 0.08 M potassium bromide. The tubes were placed on a merry-go-round apparatus and irradiated for 30 min with a 0.01 M $BiCl_3$ filter solution. The reaction mixtures were all quenched with equal amounts of water (0.5 mL) and analyzed by gas chromatography. Tube 1 produced 54% of 1-((methylsulfinyl)methyl)-1,3-diphenylindene, tube 2 produced 30%, and tube 3 produced 23% of the same product. Tube 5 produced 1-((methylsulfinyl)methyl)-1,3-diphenylindene in 6–7% yield and tube 4 1–2% yield of the same product. Tube 6 failed to produce the above products in any detectible amount.

In an additional experiment, 1,3-diphenylindenyl anion in Me_2SO when irradiated up to 3 h under the above conditions failed to show formation of 1-(methylsulfinylmethyl)-1,3-diphenylindene by gas chromatography with its limits of detection (<0.1%).

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in Tetrahydrofuran. Irradiation of the anion generated from 30.2 mg (0.1 mmol) of 2-chloro-1,3-diphenylindene, an equivalent of potassium *tert*-butoxide, and 4 mL dry tetrahydrofuran for 30 min with 0.1 M $BiCl_3$ filter solution produced 1-(2-tetrahydrofuryl)-1,3-diphenylindene (**13**, 30% after isolation and 1,3-diphenylindene (approximately 8%): NMR ($CDCl_3$) δ 7.17–7.7 (14 H, m), 6.7 (0.5 H, s, styryl), 6.5 (0.5 H, s, styryl), 4.75–5.05 (1 H, m), 3.7–3.85 (2 H, m), 1.2–1.7 (4 H, m) (the presence of half-integral proton indicated that the compound was a diastereomeric mixture); MS, *m/e*, 338 (parent), 267 (100).

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in the Presence of 1,1-Dimethoxyethylene. To the anion generated from 152 mg (0.502 mmol) of 2-chloro-1,3-diphenylindene, 1 mL of Me_2SO, and 3 mL of 0.19 M potassium *tert*-butoxide in Me_2SO was added 4–5 mL of deoxygenated 1,1-dimethoxyethylene. The reaction mixture was irradiated for 2 h at room temperature and quenched with water. Before workup, gas chromatographic analysis of the reaction mixture showed 1,3-diphenylindene (15%) and two products formed in 18% and 30% yield, respectively. After extraction with dichloromethane, drying over anhydrous magnesium sulfate, and removing the solvent in vacuo at 80 °C, gas chromatographic analysis showed the product had increased to 45–48% yield whereas 1,3-diphenylindene yield remained 15%. The reaction mixture was separated by silica gel column chromatography, eluting with hexane. Two fractions were collected. Fraction 1 (500 mL) contained 10 mg of 1,3-diphenylindene. The second fraction yielded 30 mg (20% yield) of pale yellow crystals, mp 192–195 °C, of 2-methoxy-9-phenyl-3,4-benzfluorene (**18**): NMR ($CDCl_3$) δ 8.8 (1 H, m), 8.4 (1 H, m), 7.0–7.8 (11 H, m), 6.8 (1 H, s), 5.03 (1 H, s), 3.9 (3 H); MS, *m/e* 322 (parent, 100), 307 (M − 15, 33), 291 (M − 31, 20), 276, 202; calcd for $C_{24}H_{18}O$ 322.136, found 322.124.

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in the Presence of 2,3-Dimethyl-1,3-butadiene. A 0.13 M anion solution was generated by treatment of the corresponding indene (200 mg, 0.66 mmol) with 20% excess of potassium *tert*-butoxide in 5 mL of Me_2SO. A 4–5-mL portion of 2,3-dimethyl-1,3-butadiene was added. The reaction mixture was irradiated for 2 h and quenched with water. Gas chromatographic analysis of the mixture showed 1,3-diphenylindene (10%) and two new products formed in 60% and 15–20% yield, respectively. The third product (15–20% yield) was sensitive to base concentration; its production was reduced by using equimolar potassium *tert*-butoxide. The products were separated by silica gel column chromatography (hexane). Fraction 1 (500 mL, hexane) yielded 1,3-diphenylindene and some unreacted 2-chloro-1,3-diphenylindene by gas chromatography. Fraction 2 (750 mL) yielded a glassy material (approximately 100 mg) which crystallized from ethanol. Two crystallizations from hot ethanol produced colorless needles, mp 135–137 °C, of 2,3-dimethyl-4a,9-diphenyl-1,1a,4,4a-tetrahydrofluorene: NMR ($CDCl_3$) δ 6.96–7.46 (14 H, m), 2.09 (1 H, d, *J* = 17 Hz, allylic), 2.64 (1 H, d, *J* = 18 Hz, allylic), 2.96 (1 H, d, *J* = 18 Hz, allylic), 2.14 (1 H, d, *J* = 17 Hz, allylic),[23] 1.6 (3 H, s), 1.48 (3 H, s); MS, *m/e* 348 (100), 333, 271, 255; calcd for $C_{27}H_{24}$ 348.188, found 348.188.

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in Benzene. The anion was generated from 2-chloro-1,3-diphenylindene (60.5 mg, 0.2 mmol) and a 1.0-mL Me_2SO solution (0.2 M) of potassium *tert*-butoxide. Deoxygenated benzene (4.0 mL) was added, and the solution was irradiated. Preparative silica gel thin-layer chromatography of the reaction mixture yielded 1,3-diphenylindene (20%), 1,1,3-triphenylindene (3–5%), and a hydrocarbon assumed to be the dimer of 1,3-diphenylindene (30%) by NMR (δ 6.55 (2 H, vinyl)) and mass spectral analysis. Biphenyl (5%) was also isolated from the reaction mixture; this was characterized by TLC and gas chromatographic comparison with an authentic sample of biphenyl.

Irradiation of 2-Chloro-1,3-diphenylindenyl Anion in the Presence of Dimethyl Fumarate. The anion was generated from 30.1 mg (0.1 mmol) of 2-chloro-1,3-diphenylindene with an equivalent amount of potassium *tert*-butoxide in 2.0 mL of Me_2SO. Dimethyl sulfoxide solution (5 mL) containing 73 mg (0.5 mmol) of dimethyl fumarate was added, and the reaction mixture was irradiated for 4 h. The quenched reaction mixture revealed 40–50% disappearance of 2-chloro-1,3-diphenylindene by gas chromatography. It showed formation of 1,3-diphenylindene (20–25%). No evidence of an adduct was obtained by GC and NMR analysis.

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Registry No. 1, 82190-59-8; **4a**, 91280-83-0; **4b**, 82190-60-1; **5a**, 33027-38-2; **5b**, 82190-61-2; (*R**,*R**)-**7**, 91280-86-3; (*R**,*S**)-**7**, 91280-79-4; **8**, 91280-78-3; **9(H)**, 91280-80-7; **9(D)**, 91280-82-9; (*R**,*R**)-**13**, 82992-74-3; (*R**,*S**)-**13**, 82992-75-4; **14**, 82190-66-7; (*R**,*R**)-**15**, 82190-64-5; (*R**,*S**)-**15**, 82190-65-6; (*R**,*R**)-**16**, 82190-62-3; (*R**,*S**)-**16**, 82190-63-4; **17**, 32377-10-9; **18**, 91280-84-1; **19**, 91280-85-2; **20**, 91280-77-2; $CHCl_3$, 67-66-3; $ClCH_2SCH_3$, 2373-51-5; CH_3SOCH_3, 67-68-5; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; *t*-BuOH, 75-65-0; $CH_2{=}C(OCH_3)_2$, 922-69-0; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; C_6H_6, 71-43-2; 1,1-dichloro-2,2,3-triphenylcyclopropane, 33027-37-1; triphenylethylene, 58-72-0; 1,3-diphenylindenyl anion, 90907-09-8; 3-chlorocyclohexene, 2441-97-6; 1,3-diphenyl-1-indenol, 76773-35-8; 1-chloro-1,3-diphenylindene, 91280-81-8.

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(23) Decoupling experiments confirmed that the δ 2.09 and 2.14 doublets were coupled, as were the δ 2.64 and 2.96 doublets.