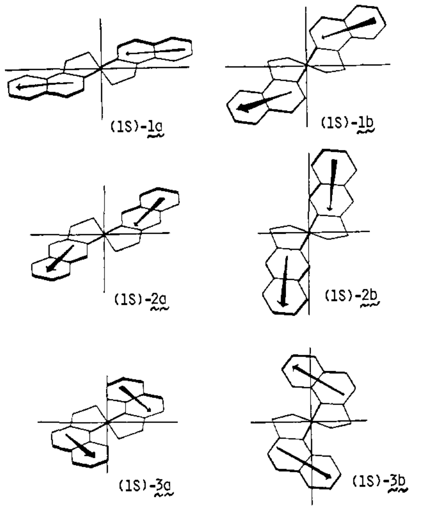
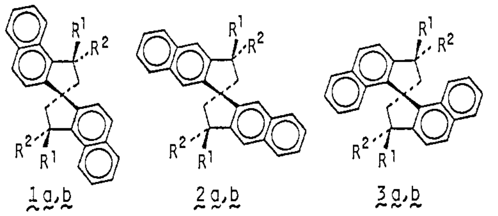


Figure 3. Lower-frequency coupling modes of the ^1B_b transition moments in 1,1′-spirobi[benzindans].

this regularity does not always hold well. Evaluation of the interaction energy V_{12} between local transition moments using the point–dipole–point–dipole approximation shows that the lower energy coupling mode can be of either symmetry, depending upon the mutual disposition of the local transition moments.[7,10]

One type of evidence corroborative of the foregoing arguments is our recent study of the three positional isomers, 3,3′-di-*tert*-butyl-1,1′-spirobi[benz[*e*]indan] (**1**),[11] -spirobi[benz[*f*]indan] (**2**),[12] and -spirobi[benz[*g*]indan] (**3**),[13] each of which includes two diastereomers with C_2 symmetry.



1a,b 2a,b 3a,b

(1S,3R,3′R)-a; $R^1 = Bu^t$, $R^2 = H$

(1S,3S,3′S)-b; $R^1 = H$, $R^2 = Bu^t$

Figure 2 shows the UV and CD spectra in the ^1B_b region[14] observed for these spiro compounds having the 1*S* configuration. According to the definition by Hug and Wagnière,[4] chirality of the chromophore is left handed for all of them. The spectral features were found to be sensitive to changes in the mutual arrangement of the local moments with a large dipole strength and a distinct polarization direction along the long axis of each naphthalene ring.[15] Since the lower energy coupling modes of local transitions located at the centers of the naphthalene rings are undoubtedly of *B* symmetry for **1a,b** and **2a,b** (V_{12}^A, ca. 1900 cm^{-1}; Figure 3, top and center),[16] the positive signs of couplets for (1*S*)-**1a,b** are obviously in conflict with the C_2 rule, while the negative ones for (1*S*)-**2a,b** are consistent with that. On the other hand, the exciton analysis can explain not only all of these CD signs but also the spectral features semiquantitatively. Thus the very weak CD of **1a** is attributable to its conformation, in which the two local moments are directed almost parallel to each other; besides, a close resemblance between the features of **2a** and **2b** agrees with the insensitiveness of the calculated rotational strength and splitting energy to the difference between their conformations.

The signs of couplets, negative for (1*S*)-**3a** and positive for (1*S*)-**3b**, are not contradictory to the C_2 rule, since the lower energy coupling mode of local transitions is of *B* symmetry for **3a** (V_{12}^A, ca. 500 cm^{-1}) and of *A* symmetry for **3b** (V_{12}^A, ca. −1300 cm^{-1}) (Figure 3, bottom). This CD behavior, however, affords a good illustration of the fact that a relatively small change in conformation causes, in some cases, the inversion of energy levels of *A* and *B* coupling and accordingly the reversal of CD signs regardless of identical chirality of the chromophore.

In conclusion, the presented results show that the C_2 rule is no longer a general one; thus, even for C_2 molecules, the determination of CD signs requires the examination of the helicity and energy relationship of transitions, as is the case for other types of chiral molecules.[7]

Registry No. 1a, 73294-82-3; **1b**, 73346-61-9; **2a**, 79264-94-1; **2b**, 79299-37-9; **3a**, 82166-56-1; **3b**, 77210-75-4.

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(9) A similar choice between two coupling modes was also made in the application of the aromatic chirality rule to some non-C_2 compounds (Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257–63).

(10) Mason, S. F.; Vane, G. W. *J. Chem. Soc. B* **1966**, 370–4.

(11) Imajo, S.; Nakamura, A.; Shingu, K.; Kato, A.; Nakagawa, M. *J. Chem. Soc., Chem. Commun.* **1979**, 868–70.

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(13) Imajo, S.; Shingu, K.; Kuritani, H. *Tetrahedron Lett.* **1980**, 4279–82.

(14) The Cotton effects observed at ca. 210 nm are possibly due to the ^1C_b transition.[15] In the UV spectrum of **1a**, the higher-frequency band with low intensity is hidden by the following ^1C_b band.

(15) (a) Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484–95. (b) Klevens, H. B.; Platt, J. R. *Ibid.* **1949**, *17*, 470–81.

(16) ^1H NMR spectroscopy showed that the dihedral angle between two aromatic planes is smaller for (1*S*,3*R*,3′*R*)-**a** (ca. 60–75°) than for (1*S*,3*S*,3′*S*)-**b** (ca. 90–110°), owing to the opposite sense of puckering of the five-membered rings in which the *tert*-butyl groups tend to assume quasi-equatorial orientations for each diastereomer.[11-13]

Carbanion Photochemistry. 6. Formation of a Reactive Carbene via Photoinduced Halide Elimination[1]

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Although cyclopentadienylidene[2] and various phenylated derivatives,[3a-f] as well as the 2,3-benzo[3g,h] and 2,3,4,5-dibenzo derivatives[3i,j] have been synthesized and studied, the corresponding 3,4-benzo derivative has not. For this carbene, the electronic demand from two potentially aromatic rings should favor mixing in of states containing electrons in the formal p orbital. We now report evidence for the synthesis of 1,3-diphenylisoindenylidene (**1**) using a novel photoelimination reaction from a carbanion. Unlike other members of this series, this carbene undergoes hydrogen atom abstraction in preference to addition.

Simple Hückel molecular orbital theory predicts an increased electron density at the C-2 position of photoexcited allyl anions. Thus a 2-bromo-substituted allyl anion should undergo photoelimination provided the ground-state elimination is avoided. The 2-bromo-1,3-diphenylindenyl anion (**2a**), although only formally an allyl anion, is known to be thermally stable[4] and satisfies the Hückel model for increased C-2 electron density in the excited state.

Solutions of the requisite anion (ca. 0.1 M) were produced by 10% excess potassium *tert*-butoxide treatment of 2-bromo- or 2-chloro-1,3-diphenylindene[4] in dimethyl sulfoxide. A 10-fold

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(1) For previous papers, see: (a) Tolbert, L. M.; Merrick, R. D. *J. Org. Chem.* **1982**, *47*, 2808. (b) Tolbert, L. M.; Siddiqui, S. *Tetrahedron* **1982**, *38*, 1079.

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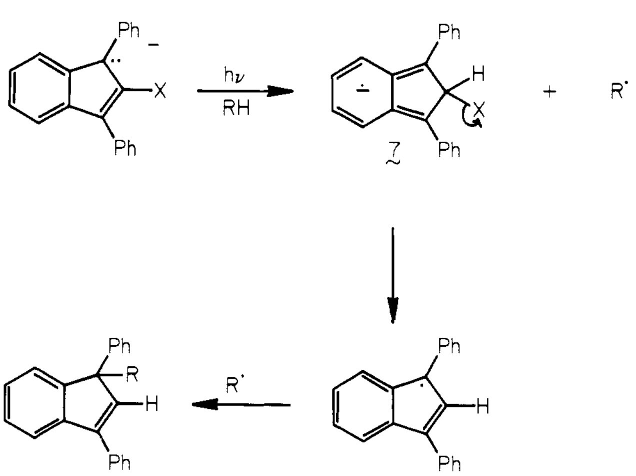
(4) Koelsch, C. F. *J. Org. Chem.* **1960**, *25*, 130.

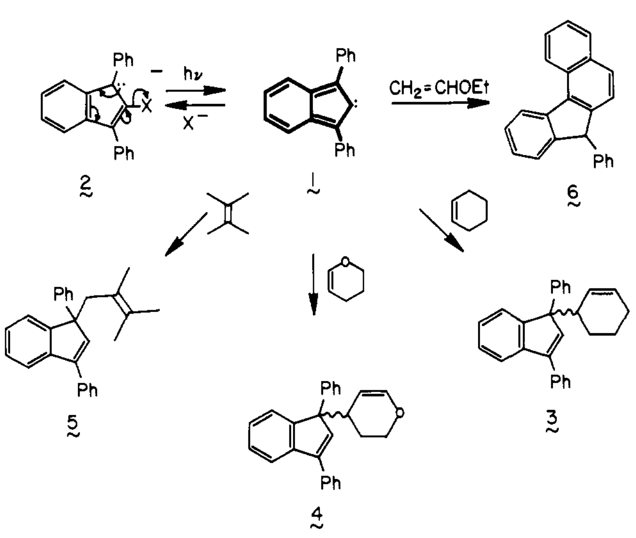
Scheme I. Hydrogen Abstraction as the Primary Process



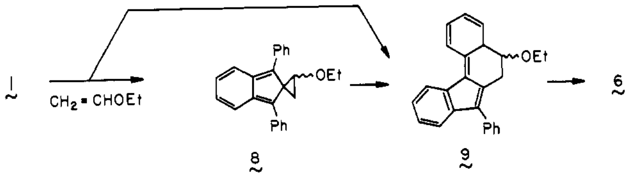
excess of an olefin was added, and the mixture was irradiated with $BiCl_3$-filtered (>350 nm) Hanovia light. Reactions were monitored by gas chromatography and carried to ca. 60–90% conversion. The mixtures were quenched with water and extracted with methylene chloride, and the products were separated by column chromatography. The major product in each case was isolated in over 50% yield as a colorless oil and exhibited a molecular ion in the mass spectrum corresponding to the loss of halogen and addition of the olefin. The case of cyclohexene is particularly instructive. In addition to aromatic peaks, the NMR showed absorbances in the styryl, olefinic, allylic methine, and ring methylene regions.[5] The number of protons of each type and the presence of half-integral protons indicated that the compound was a 50:50 mixture of diastereomeric 1-(cyclohex-2-enyl)-1,3-diphenylindenes (**3**). This structure was confirmed by elemental analysis and independent synthesis. Thus addition of 3-chlorocyclohexene to 1,3-diphenylindenyl anion in Me_2SO produced a 60:40 mixture of the same diastereomers in 60% yield after chromatography. Dihydropyran also produced a similar product, 1-(4-oxacyclohex-2-enyl)-1,3-diphenylindene (**4**)[6] as a mixture of diastereomers remarkable for the γ insertion into the dihydropyran moiety, while the adduct with 2,3-dimethylbutene, 1-(2,3-dimethylbut-2-enyl)-1,3-diphenylindene (**5**),[7] showed the expected AB quartet for the diastereotopic allylic methylene protons. In each case, 1,3-diphenylindene was a minor (<10%) product. In contrast, ethyl vinyl ether produced no insertion product but rather the product of addition–elimination, 9-phenyl-3,4-benzofluorene (**6**).[8]

A possible mechanism for the C–H insertion product involves hydrogen atom abstraction by the photoexcited carbanion, a known reaction,[9] followed by loss of halogen (see Scheme I). However, in extensive studies on the 1,3-diphenylindenyl anion itself we have failed to detect products of hydrogen atom abstraction.[1b] Moreover, the 2-chloro anion **2b** disappears at least 4 times faster than the 2-bromo anion **2a**, a result that is difficult to rationalize with the intermediacy of radical anion **7** assuming similar excited state lifetimes, i.e., radical anions of haloaromatics exhibit reactivity of the order $I^- > Br^- \gg Cl^-$.[10] Finally, the photochemistry of the 2-chloro anion was effectively quenched by a factor of 2 in the presence of 0.06 M potassium chloride or bromide. In the latter case, the bromoindene conjugate acid of **2a** was formed through halogen exchange, a known reaction of carbenes.[11] Thus loss of halide appears to be a primary photochemical process, a result that is consistent with the intermediacy of 1,3-diphenylisoindenylidene, **1** (see Scheme II).).

Scheme II. Products from Reaction with Photoexcited **2**



Scheme III. Mechanisms for 9-Phenyl[3,4]benzofluorene Formation



Products analogous to **6** have been observed previously in the reaction of 2,3,4,5-tetraphenylcyclopentadienylidene with acetylenes[12] and may rise via the intermediate benzospiro[2.4]heptadiene **8** or from the product of the novel 2 + 7 cycloaddition, polyene **9** (see Scheme III).

The propensity for H atom abstraction rather than double-bond addition is in contrast to other carbenes of this series, although H atom abstraction has been observed for singlet carbenes.[13] The lack of a cyclopropanation product probably reflects the instability of the resulting spiro intermediate of type **8**. We have obtained addition products from olefins not containing abstractable protons and have found, in most cases, complex isomeric addition products.

Halide elimination from carbanions provides a further deactivation pathway for photoexcited carbanions in addition to the more conventional photoejection pathways. Moreover, the use of photopromoted halide elimination may provide a new source of reactive carbenes when the traditional diazo precursors are synthetically unavailable.

Acknowledgment. Support by the Research Corp. and the Office of Basic Energy Sciences, U.S. Department of Energy, is gratefully acknowledged.

Registry No. **1**, 82190-59-8; **2a**, 82190-60-1; **2b**, 82190-61-2; (*R**,*R**)-**3**, 82190-62-3; (*R**,*S**)-**3**, 82190-63-4; (*R**,*R**)-**4**, 82190-64-5; (*R**,*S**)-**4**, 82190-65-6; **5**, 82190-66-7; **6**, 32377-10-9; cyclohexene, 110-83-8; dihydropyran, 110-87-2; ethyl vinyl ether, 109-92-2; 2,3-dimethylbutene, 563-79-1.

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(5) NMR ($CDCl_3$) δ 7.1–7.7 (14 H, m, Ar), 6.6 (1 H, two overlapping s, styryl), 5.68 (1 H, s, isomer A, vinyl), 5.46–5.65 (0.5 H, m, isomer B, vinyl), 5.05–5.3 (0.5 H, d, isomer B), 3.2–3.5 (1 H, m), 1.4–2.0 (6 H, m, methylene); MS, 267 (100%), 265, 91, 84, 81, confirmed by independent synthesis, elemental analysis, and exact mass determination.

(6) NMR ($CDCl_3$) δ 7.15–7.8 (14 H, m, Ar), 6.8 (0.5 H, s, isomer A, styryl), 6.6 (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_2O and methine), 1.8–2.5 (2 H, M, methylene); MS, 350, 267, 265, 83, the exact mass was consistent with the assumed formula.

(7) NMR ($CDCl_3$) δ 7.1–7.7 (14 H, m, Ar), 6.6 (1 H, Hz, s, styryl), 3.18–3.33 (1 H, d, J = 13 Hz, methylene), 2.85–3.0 (1 H, d, J = 13 Hz, methylene), 1.6 (6 H, s, CH_3), 1.3 (3 H, s, CH_3); MS, 250, 267, 265, 190, 83, the exact mass was consistent with the assumed formula.

(8) Confirmed by MS (292.215), elemental analysis, and its reported melting point and NMR: Dufour, M.; Perin, F.; Jacquignon, P. *Bull. Soc. Chim. Fr.* **1973**, 3166.

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