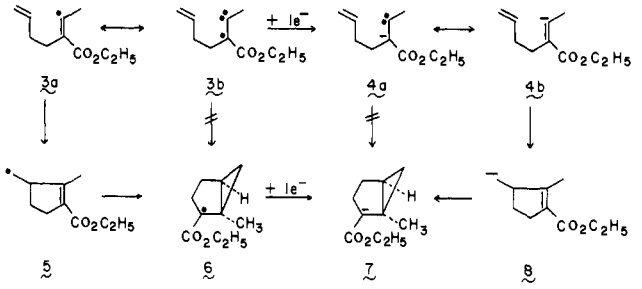
100 and 130 mA. After all of **1** had been added, the applied potential was increased to −2.30 V and maintained at this level until the current dropped below 10 mA. The reaction mixture was diluted with pentane and washed successively with 5% aqueous hydrochloric acid, water, and brine. After drying, the pentane solution was concentrated, and the product was isolated from the residue by medium pressure liquid chromatography to yield 58% of **2**.[8]

Table I lists the products and yields obtained for the reductive double cyclizations of a series of β-dicarbonyl enol phosphates. The first two examples from the table illustrate that both esters and ketones can function as the residual carbonyl containing group. The third example illustrates six-membered ring formation. Examples four and five show that the substitution patterns can be readily varied, while example eight illustrates the use of this cyclization for the formation of a tricyclic ester. Although the final protonation had been very stereoselective in examples one through three, example eight showed almost complete loss of stereoselectivity in the final addition of hydrogen, which indicates that protonation is comparably hindered from both faces of the cyclopentyl ring.

The mechanism of this reaction is complex and cannot be rigorously defined at this time. Structures **3** and **4** represent the



transitory intermediates which would result from the one-electron and two-electron reductions, respectively, of **1**, coupled with the loss of the diethyl phosphate anion. The singlet carbene **4a** is a resonance structure of the vinyl anion **4b**, and **3b** is a resonance structure of **3a**. Several mechanistic possibilities exist. Cyclization of **3a** to give **5**, followed by a second cyclization to yield **6**, and subsequent reduction would produce **7**.[9] Carbene addition via **3b** would give **6** directly. Reduction of **3** would produce **4**, which could give **7** in either a two-step anionic process involving initial formation of **8** followed by intramolecular Michael addition or by an intramolecular carbene addition.

In order to establish that a singlet carbene addition was not involved, examples six and seven of Table I were run. These reactions demonstrated that the addition to the double bonds of the two starting materials occurred with the loss of stereochemical integrity. This would appear to exclude singlet carbenes such as **3a** or **4a** as reactive intermediates.[10] These two reactions illustrate that even though an intermediate is formed which allows isomerization to occur, the reactive intermediate must be short-lived since complete equilibration does not occur.[11-13]

In summary, an unprecedented electrochemical reduction of β-dicarbonyl enol phosphates[14] to bicyclo[*n*.1.0]alkanes has been developed.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

(8) In addition to 58% of **2**, approximately 19% of a four-electron reduction product (saturated monocarbonyl derivative) was obtained. The overall consumption of electrons was 2.4-3.0 Faradays per mole of β-dicarbonyl enol phosphate reduced in examples one through eight of Table I.

(9) Direct hydrogen abstraction by **6** to give **2** must also be considered as a possibility.

(10) This loss of stereochemistry requires the presence of an intermediate in which one bond has been formed to the pendant double bond to form a new intermediate, in which rotation can occur to give loss of stereospecificity. This is inconsistent with the addition of a singlet carbene to the double bond but would be compatible with radical cyclization, anionic attack, or addition of a triplet carbene.

(11) Double cyclization of vinyl radicals via intermediates analogous to **5** and **6** have been postulated previously in the literature.[2] However, *analogous cyclopropane derivatives have not been isolated.* In our examples, cyclopropane derivatives may be isolable due to the stabilization of both **6** and **7** by the attached carbonyl group.

(12) The reduction of **5** to **8** prior to the second cyclization reaction must also be considered. However, the short lifetime of the intermediate (ring closure competitive with bond rotation) makes this possibility unlikely.

(13) Examples six and seven of Table I also provide evidence against the formation of vinyl anions, such as **4b**, as intermediates in the double cyclization process. It has been noted that vinyl anions do not add intramolecularly to unactivated 1,2-disubstituted alkenes at a useful rate. For a pertinent discussion, see: Chamberlin, A. R.; Bloom, S. H.; Cervini, L. A.; Fotsh, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 4788. Bailey, W. F.; Patricia, J. J.; Nurmi, T. T. *Tetrahedron Lett.* **1986**, *27*, 1865.

(14) This reductive cyclization was not restricted to β-dicarbonyl enol phosphates. When the ethyl carbonate of the β-dicarbonyl enol corresponding to the β-dicarbonyl enol phosphate used in example five was electrochemically reduced under the normal reaction conditions, a 43% yield of the same product was obtained.

Absence of Conformational Dependence of Norrish II Biradical Lifetimes

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A few years ago we suggested, based on the direct observation of Norrish II biradicals from (gauche-locked) *cis*-1-benzoyl-2-benzhydrylcyclohexane and from (unconstrained but anti-biased) γ,γ-diphenylbutyrophenone,[1] that there was little or no dependence of lifetime of such 1,4 biradicals on conformation around the 2,3 bond. Subsequently, Johnston, Scaiano, Sheppard, and Bays[2] reported the photochemistry and transient spectroscopy of 1-benzoyl-2,2-dimethylcyclopropane (**1-H**) and diethyl analogue **1-Me**. Lifetimes reported for transients from **1-H** and **1-Me**, assigned as Norrish II biradicals, were in the range of 20 ns, a factor of 5 shorter than that for unconstrained but comparably substituted Norrish II biradicals in the same solvent (methanol). This result was presumed to reflect the short distance between the termini in biradicals **2-H** and **2-Me**, locked as eclipsed around the bond of interest, since it would have been consistent with the general proposition[3-5] that closer termini imply larger spin-orbit coupling, and thus faster intersystem crossing (isc) and shorter lifetimes. We now present evidence in favor of an alternate interpretation of the result, specifically that an adiabatic opening occurs prior to intersystem crossing of (cyclopropyldicarbinyl) biradicals **2-H** and **2-Me**. That, and not accelerated isc, is responsible for the attenuated lifetime. We have prepared the dibenzyl derivative **1-Ph**, which in contrast to **1-H** and **1-Me** affords a Norrish II biradical **2-Ph** with lifetimes very similar to those for an unconstrained model. Thermochemical considerations suggest that **2-H** and **2-Me** can, but **2-Ph** cannot, undergo adiabatic ring opening.

Photolysis through Pyrex of **1-Ph**, mp 74-75 °C,[6] affords two products in either methanol or benzene. One, a colorless oil, is

(1) Caldwell, R. A.; Dhawan, S. N.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 6459.

(2) Johnston, L. J.; Scaiano, J. C.; Sheppard, J. W.; Bays, J. P. *Chem. Phys. Lett.* **1986**, *124*, 493.

(3) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(4) Mizuno, K.; Ichinose, N.; Otsuji, Y.; Caldwell, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5797. Barton, D. H. R.; Charpiot, B.; Ingold, K. U.; Johnston, L. J.; Motherwell, W. B.; Scaiano, J. C.; Stanforth, S. C. *J. Am. Chem. Soc.* **1985**, *107*, 3607.

(5) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 3618. Zimmt, M. B.; Doubleday, C., Jr.; Gould, I. R.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724.

(6) The synthesis of 1-Ph was analogous to that in ref 2 for **1-H** and **1-Me** and will be described elsewhere.

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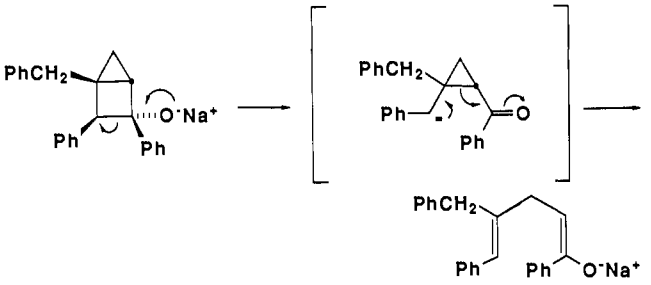
a 1:1 *E*:*Z* mixture of the 4-benzyl-1,5-diphenyl-4-penten-1-one isomers[7] (**3-Ph**), analogous to **3-H** and **3-Me**, the fragmentation products reported previously.[2] The other is assigned as 1-benzyl-*exo*,*exo*-2,3-diphenylbicyclo[2.1.0]pentan-3-ol (**4**), mp 88–89 °C, on the basis of spectral properties,[8] particularly by comparison of the ^{1}H NMR to that of the known[9] *exo*,*exo*-2,3-diphenylbicyclo[2.1.0]pentane, and on the basis of its facile conversion by NaH in refluxing toluene to one of the isomers of **3-Ph**, presumably by the mechanism

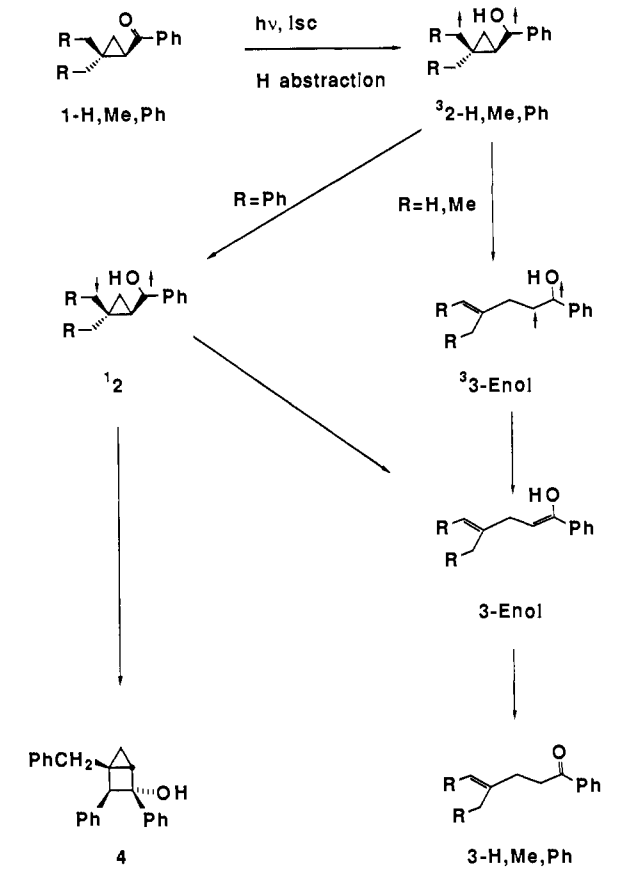


Observation of both fragmentation and closure products is consistent with a Norrish II biradical precursor. Yields in MeOH were 50% for **3-Ph** and 30% for **4** and in benzene 50% for **3-Ph** and 16% for **4**. In contrast, the photochemistry of **1-H** and **1-Me** was reported to be exclusively scission.[2] We have examined **1-Me** photolysis carefully, and we also find no (<2%) bicyclopentanol product. Cyclobutanol yields for Me (18%) vs Ph (11%) at the γ position of butyrophenone[10] show that the difference is not ascribable to the substituent. Gauche or eclipsed conformations of otherwise unconstrained Norrish II biradicals are expected to afford closure as a significant and perhaps the major product.[1,11]

Transient spectroscopy of **1-Ph** and **1-Me** was performed at 266 nm (Nd-YAG fourth harmonic, ca. 2 mJ, 10 nsec pulse width) with the following results: **1-Ph**, τ(MeOH) 117 ± 3 ns; τ(heptane) 34 ± 1 ns; no λ_{max} > 290 nm;[12] **1-Me**, τ(MeOH) 13 ns; τ(heptane) 10 ns; no clear λ_{max} > 290 nm. Results for **1-Ph** are very similar to those for γ-phenylbutyrophenone,[13] the Norrish II biradical from which shows τ(MeOH) 130 ns and τ(heptane) 53 ns. The results for **1-Me** are in qualitative agreement with those of Scaiano.[2]

The following line of reasoning convinces us that the transient lifetime from **1-Me** does not represent rate-limiting isc of a Norrish II biradical. First, there is no precedent for a difference of this magnitude in isc rate between γ-aryl and γ-alkyl substituted Norrish II biradicals.[13b] Since **2-Ph** lifetime and chemistry are both in accord with precedent, we seek explanation of unusual behavior in **2-H** and **2-Me**. Second, the absence of closure product

Scheme I



from **1-H** and **1-Me** but not from **1-Ph** has no ready explanation if isc is from ^{3}**2** to ^{1}**2** for all three. Third, the ring opening of cyclopropylcarbinyl radical to 3-butenyl is very fast at room temperatures (lifetime ca. 10 ns), with $\Delta H°$ determined to be −4 ± 1 kcal/mol,[14] and the similarity of this lifetime to that of **2-Me** is striking. Corresponding openings for **2-H** and **2-Me** should be very similar thermochemically. The –C(OH)Ph terminus will have little thermochemical impact: we have recently shown[15] that olefin triplets, cf. ^{3}**3-Enol**, are thermodynamically well modeled as 1,2-biradicals, i.e. the thermochemical contribution of the terminus will not differ much between **2** and ^{3}**3-Enol**. Kinetically, ^{3}**2** has an eclipsing interaction that might even accelerate a cleavage. The adiabatic opening should therefore be expected, and adiabatic opening of cyclopropyl-containing biradicals has in fact been previously reported.[16] *We suggest similar adiabatic openings for* **2-H** *and* **2-Me**, *which then would readily explain both the absence of cyclobutanol and the short lifetimes.* Why, then, does **2-Ph** not open? *The extra resonance stabilization of ca. 13 kcal/mol at the benzylic terminus should simply render the adiabatic opening some 8–9 kcal/mol endothermic.*[17] The scheme below summarizes the chemistry. It has the advantage that the choice between the two paths is not arbitrary but is predicted from the thermochemistry. We cannot distinguish between ^{3}**2-Me** and

(7) All compounds gave the correct C–H analysis; the ketone **3-Ph** had a ^{1}H NMR spectrum analogous to that reported for **3-Me** in ref 2.

(8) IR 3561 cm^{-1} (OH), no C=O; ^{1}H NMR ($CDCl_3$, 200 MHz) 7.49–7.05 (m, 15 H), 3.67 (s, 1 H), 3.28 (d, J = 14.16 Hz, 1 H), 3.13 (d, J = 14.16 Hz, 1 H), 2.17 (d, 1 H, J = 5.90 Hz), 1.66 (s, 1 H, disappears on D_2O addition), 1.28 (d, J = 5.37 Hz, 1 H), 1.01–0.98 (m, 1 H); ^{13}C NMR (δ vs TMS) 147.66, 139.13, 136.62, 129.50, 128.51, 128.33, 126.81, 126.46, 124.59, 72.73, 55.56, 38.68, 26.81, 25.02, 16.03.

(9) Block, E.; Orff, N. W.; Winter, R. E. K. *Tetrahedron* **1972**, *28*, 4496. Wiberg, K. B.; Barth, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 1969.

(10) Scaiano, J. C.; Lissi, E. A.; Encina, M. V. *Rev. Chem. Intermed.* **1978**, *2*, 139–196 and references therein, esp.: Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.

(11) See: Zimmerman, R. G.; Liu, J. H.; Weiss, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 5264. Scheffer, J. R.; Trotter, J. *Rev. Chem. Intermed.* **1988**, *9*, 271–305. Ariel, S.; Evans, S. V.; Garcia-Garibay, M.; Harkness, B. R.; Omkaram, N.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1988**, *110*, 5591. However, see Lewis et al. (Lewis, F. D.; Johnson, R. W.; Ruden, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 4292. Lewis, F. D.; Johnson, R. W.; Johnson, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 6090) for gauche-locked cases in which (among the Norrish II products) α-methylation causes exclusive cyclobutanol formation but in its absence exclusive fragmentation occurs.

(12) Transient lifetime was unquenched by isoprene but the intensity was quenched, consistent with quenching of the triplet precursor to the observed transient.

(13) (a) Caldwell (Caldwell, R. A. *Pure Appl. Chem.* **1984**, *56*, 1187) shows the values given here which supersede the initial values in: (b) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629.

(14) Carter, W. P. L.; Tardy, D. C. *J. Phys. Chem.* **1979**, *78*, 1295. Effio, A.; Griller, D.; Ingold, K. V.; Beckwith, A. L. J.; Serelis, A. U. *J. Am. Chem. Soc.* **1980**, *102*, 1734. See also: Quenemoen, K.; Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1985**, *107*, 5059.

(15) Ni, T.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.*, in press.

(16) Adam, W.; Hannemann, K.; Hössel, P. *Tetrahedron Lett.* **1984**, *25*, 181. Adam, W.; Günther, E.; Hössel, P.; Platsch, H. *Tetrahedron Lett.* **1987**, *28*, 4407. See also Nishino et al. (Nishino, H.; Toki, S.; Takamuku, S. *J. Am. Chem. Soc.* **1986**, *108*, 5030) for adiabatic ring opening of a quadricyclane derivative which, if stepwise, would provide an even closer analogy.

(17) The lower number considers delocalization in the ground-state styrenic terminus. A styrene delocalization energy of about 1 kcal/mol relative to noninteracting benzene and ethylene was derived from heats of hydrogenation: Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; John Wiley and Sons, Inc.: New York, 1961; p 243.

^{3}**3-Enol** for the short-lived transient from **1-Me**, and we expect it is probably an evolving mixture of the two.

Several conclusions may be drawn. Most importantly, the role of conformational control of interterminal distance in determining intersystem crossing rates of Norrish II 1,4 biradicals is indeed small and does contrast with experiments in which the interterminal distance is varied by varying the number of intervening bonds[3,4] or with cases in which through-space interaction dominates.[3,5] It seems likely that through-bond effects dominate the spin-orbit coupling interaction in the present case. Second, there is no special role of the cyclopropyl spacer in intersystem crossing; its special role is in facilitating the adiabatic scission thermochemically. Since ^{3}**2** is formally a cyclopropylcarbinyl biradical of the sort proposed in triplet state di-π-methane reactions,[18] we suggest that the dynamic behavior of such biradicals will not be exceptional, but can be understood on the basis of intersystem crossing and thermochemical kinetics of simpler biradical models. Third, the adiabatic opening of **2-Me** would suggest that triplet state cyclopropyldicarbinyl biradical formation from olefin triplet precursors is likely also adiabatically reversible when thermodynamically acceptable.

We will report separately the findings for another series of 1,4-biradicals which demonstrates a similar absence of conformational dependence.[19]

Acknowledgment is made to the Robert A. Welch Foundation (Grant AT-532) and the National Science Foundation for financial support. Laser flash photolysis was performed at the Center for Fast Kinetics Research at The University of Texas at Austin, supported by Grant RR-00886 of the Biotechnology Branch of the Division of Research Resources of the National Institutes of Health and by the University of Texas. S.C.G. thanks Kurukshetra University, India, for granting sabbatical leave.

(18) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718. Zimmerman, H. E.; Armesto, D.; Mercedes, G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367.

(19) Caldwell, R. A.; Sink, R. M. Manuscript in preparation.

Chiral Azophenolic Acerands: Color Indicators To Judge the Absolute Configuration of Chiral Amines†

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Chiral azophenolic acerands[1e] **1-3**[2] are particularly interesting molecules because of their two different functions, enantiomer differential complexation established by Cram and his co-workers[3] and guest-selective coloration,[1] in the same molecule. These

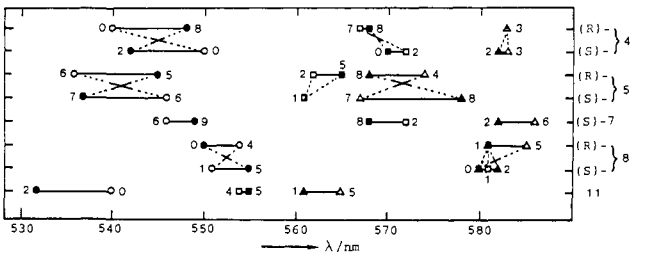


Figure 1. Absorption maxima for the colored salts of **1-3** with chiral amines in ethanol. The number next to the symbol is the units digit for the value of λ_{max}: (△), salt of (*RR*)-**1**; (▲), (*SS*)-**1**; (○), (*RRRR*)-**2**; (●), (*SSSS*)-**2**; (□), (*RR*)-**3**; (■), (*SS*)-**3**.

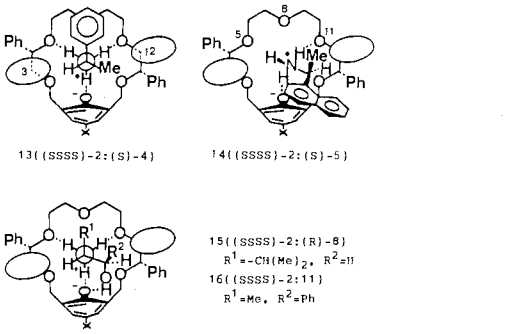
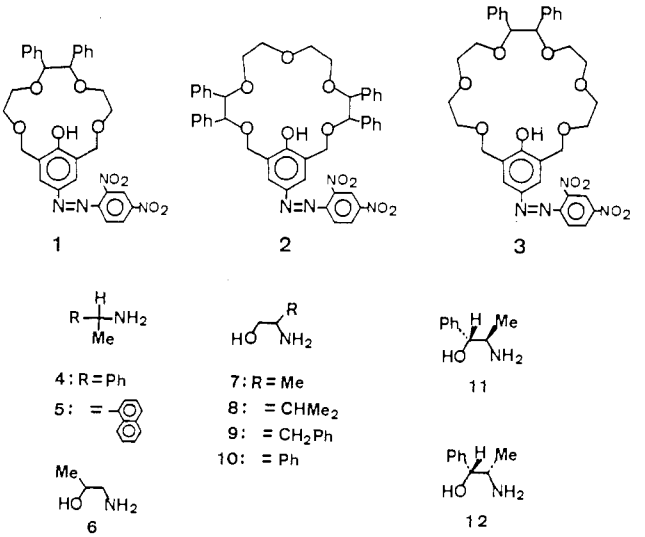


Figure 2. Predicted structures of the saltexes consisting of **2-4**, **-5**, **-8** and **-11** combinations, where X = 2,4-dinitrophenylazo group. The Ph groups at C_3 and C_{12} are shown as ellipses.

chromoacerands provide a good model to examine enantiomeric amine-selective coloration, the observation of which must be the first step toward developing color indicators to judge the absolute configuration of chiral amines on the basis of host-guest saltexing.[1e] We report here the first successful approach to such color indicators.[4]

Thirteen chiral amines **4-12** including four enantiomeric pairs



of alkyl- and ethanolamines **4-6** and **8** were used as potential guests. These colorless species were treated in ethanol with three enantiomeric pairs of yellow indicators **1-3** to give 39 diastereomeric sets of purple-colored ammonium phenolates, whose visible spectra were determined.[5] The absorption maxima for

† Dedicated to Professor Donald J. Cram, UCLA, on the occasion of his 70th birthday.

(1) For metal-ion-selective coloration: (a) Kaneda, T.; Sugihara, K.; Kamiya, H.; Misumi, S. *Tetrahedron Lett.* **1981**, *22*, 4407-4408. (b) Sugihara, K.; Kaneda, T.; Misumi, S. *Heterocycles* **1982**, *18*, 57-61. (c) Tanigawa, I.; Tsuemoto, K.; Kaneda, T.; Misumi, S. *Tetrahedron Lett.* **1984**, *25*, 5327-5330. (d) Kaneda, T.; Umeda, S.; Tanigawa, H.; Misumi, S.; Kai, Y.; Morii, H.; Miki, K.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 4802-4803. For amine-selective coloration: (e) Kaneda, T.; Ishizaki, Y.; Misumi, S.; Kai, Y.; Hirao, G.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 2970-2972. (f) Kaneda, T.; Umeda, S.; Ishizaki, Y.; Kuo, H.-S.; Misumi, S.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.*, in press. For reviews: (g) Misumi, S.; Kaneda, T. *Mem. Inst. Sci. Ind. Res., Osaka Univ.* **1987**, *44*, 29-47. (h) Kaneda, T. *J. Synth. Org. Chem., Jpn.* **1988**, *46*, 96-107.

(2) Hirose, K. Ph.D. Thesis, Osaka University, 1988. Acerands **1-3** were synthesized via quinone intermediates by a method similar to that described previously.[1] The synthetic work will be reported elsewhere.

(3) (a) Kyba, E. B.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 2692-2693. (b) Cram, D. J.; Helgeson, R. C.; Sousa, L. R.; Timko, J. M.; Newcomb, M.; Moreau, P.; de Jong, F.; Gokel, G. W.; Hoffman, D. H.; Domeier, L. A.; Peacock, S. C.; Madan, K.; Kaplan, L. *Pure Appl. Chem.* **1975**, *43*, 327-349.

(4) For the first report on this subject, see: Hollmann, G.; Vögtle, F. *Chem. Ber.* **1984**, *117*, 1355-1363.

(5) The stock solutions of an enantiomeric pair of the indicators were prepared carefully so that their concentrations (ca. 10^{-5} M) were exactly the same. Commercially available chiral amines were used without further purification after checking the rotation. An indicator/amine molar ratio of $1:10^3$ was employed for all cases. The acerands dissociate to some extent in ethanol, so that two absorption bands due to the phenol and the phenolate appear at 390 and 587 for **1**, 397 and 555 for **2**, and 393 and 582 nm for **3**, respectively.

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