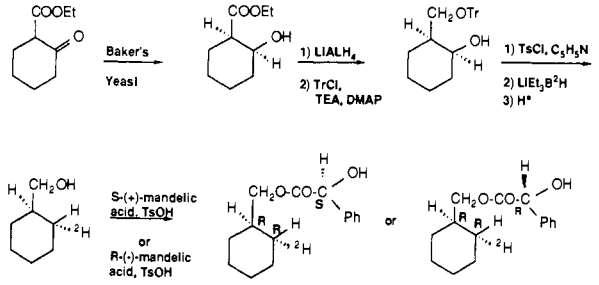
Scheme II. Synthesis of (1*R*,2*R*)-[2-$^2H_1$]Cyclohexylcarbinol *R*-(−)- and (*S*)-(+)-Mandelate Ester



derivative and 0.29 ppm ($\Delta^2H - \Delta\delta_{C\text{-}2/C\text{-}6}$) in the *R*-(−)-mandelate ester, indicating that in the *S*-(+)-mandelate ester the lower field (δ 29.38 ppm) signal originates from C-6 (the *pro*-S carbon) and the higher field signal (δ 29.33 ppm) from C-2 (*pro*-*R* carbon). The assignment is most easily deduced from the signal pattern of a 2:1 mixture of the *R*-(−) and the *S*-(+) esters [Figure 1D].

The stereochemical assignment shows that C-2 of shikimate gives rise to C-6 of the cyclohexanecarboxylic acid moiety of **1**. This finding agrees with the steric course of cyclohexane ring formation in the biosynthesis of ω-cyclohexyl fatty acids deduced by Okuda and co-workers.[27] While this result has been interpreted to indicate a direct double bond reduction of shikimic acid on the *re* face,[27] the observed stereochemical outcome may well be the result of a much more complex sequence of events. This possibility is suggested by the observation that D-(−)-[6-$^2H_1$]shikimic acid (98% ^2H, 6*R*:6*S* 2:1)[28] fed to *S. collinus* (50 mg/L) gave no detectable (<0.1%) deuterium incorporation into **1**, indicating complete loss of both methylene hydrogens of **2** in the conversion.

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Divergent Photochemistry of 2,4-Di-*tert*-butylacetophenone and -benzophenone

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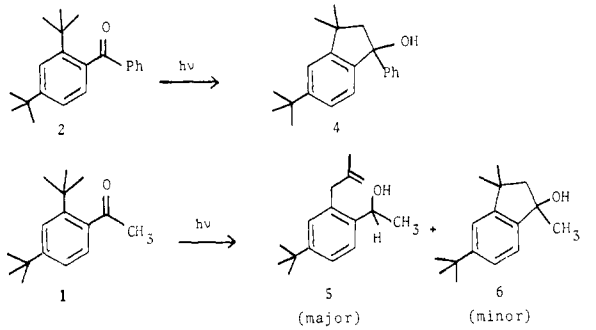
We have already reported that *o*-alkoxyacetophenones and benzophenones behave quite differently photochemically and ascribed the differences to differing rotational freedom in the 1,5-biradical intermediates formed from the ketone triplets.[1] We have now found an even more dramatic contrast between the photobehavior of *o*-*tert*-butylacetophenones and benzophenones that appears to verify the importance of rotational freedom in determining product ratios in the reactions of biradicals with benzylic centers.

Both 2,4-di-*tert*-butylacetophenone (**1**) and 2,4-di-*tert*-butylbenzophenone (**2**) were prepared by Friedel-Crafts acylation of 1,4-di-*tert*-butylbenzene. Their structures were determined by X-ray crystallography.[2] They share an important structural feature with *o*-*tert*-butylbenzophenone (**3**),[3] namely a 68-70° dihedral angle between the dibutylphenyl ring and the carbonyl.



Irradiation of **2** in several solvents produces only indanol **4** in a reaction completely analogous to that of **3**. The quantum yield varies from 0.03 (hexane) to 1.0 (methanol). Triplet lifetimes were measured by flash kinetics[4] and are 1.7 ns in toluene and 3.3 ns in methanol at 25°, some 3 times longer than for **3**. The reaction is readily quenched by conjugated dienes, with $k_q\tau$ values of 6.5 in hexane and 20 in methanol, corresponding to k_q values of 4-6 × 10^9 M^{-1} s^{-1}, a very normal range.[5]

Irradiation of **1** in several solvents produces primarily an internal redox product **5**,[6] with only 5-10% of indanol **6**[7] as a byproduct. Total quantum yields are only 0.02-0.05 in benzene and methanol. Triplet lifetimes are 25 ns in toluene and 130 ns in methanol.[8] The reaction is barely quenchable in hydrocarbon solvents, and k_q for 2,4-hexadiene in methanol is only 2 × 10^8 M^{-1} s^{-1}. The same value was determined by measuring sensitized yields of triplet 1-methylnaphthalene.[9]

It remains to be explained why triplets **1** and **2** undergo triplet energy transfer at such different rates and why they give such different products. We believe that both differences arise from triplet **1** having a considerably smaller dihedral angle between the carbonyl and the dibutylbenzene ring than is the case for its ground state and for all states of **2** and **3**. The solvent effect on reactivity indicates that the lowest triplet of **1** is π,π^*,[10,11] as expected from the known effect of dimethyl substitution.[10] π conjugation is far more important in excited states than in ground states,[12] so it is expected that the carbonyl of **1** would conjugate more with the benzene ring in the triplet than in the ground state. In **2** and **3**, the other benzene ring is available for conjugation with the carbonyl, so that the o-*tert*-butyl group remains rotated away from the carbonyl in the triplet state. The slow triplet energy transfer from triplet **1** presumably reflects the in-plane o-*tert*-butyl

(1) Wagner, P. J.; Meador, M. A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7988.

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(6) 2-Methyl-3-(2-(1-hydroxyethyl)-4-*tert*-butylphenyl)propene was isolated by chromatography on silica gel: IR (CCl_4) 3610, 3080, 2975, 2940, 2915, 2880, 1635, 1010, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.46 (d, 1 H, *J* = 8.2 Hz), 7.29 (d of d, 1 H, *J* = 8.2, 2.2 Hz), 7.13 (d, 1 H, *J* = 2.2 Hz), 5.08 (quartet, 1 H, *J* = 6.4 Hz, C*H*(CH_3)-OH), 4.82 (s, 1 H, vinyl), 4.48 (s, 1 H, vinyl), 3.38 (s, 2 H, CH_2), 1.76 (s, 3 H, C=C-CH_3), 1.72 (s, 1 H, exchangeable OH), 1.45 (d, 3 H, *J* = 6.4 Hz, CH(OH)-CH_3), 1.31 (s, 9 H, *t*-Bu); MS, *m/e* 232, 217, 199, 157, 143, 91, 77, 57 (100).

(7) 1,3,3-Trimethyl-5-*tert*-butyl-1-indanol isolated by chromatography on silica gel: ^1H NMR ($CDCl_3$) δ 7.13-7.48 (m, aromatic), 2.07 (d, 2 H, *J* = 1.55 Hz (collapsed AB quartet), CH_2), 1.35 (s, 9 H, *t*-Bu), 1.32 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3); MS, *m/e* 214, 199 (100), 184, 158, 143, 128, 57.

(8) This change corresponds to the sixfold decrease in the rate constant for γ-hydrogen abstraction by triplet 2,4-dimethylvalerophenone in *tert*-butyl alcohol compared to benzene.[10]

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(12) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820.

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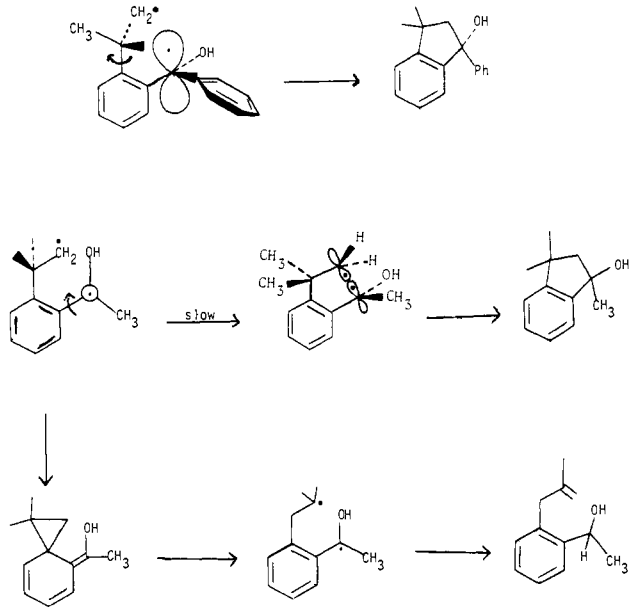
group strongly hindering approach to the carbonyl n-orbital.

The internal redox photochemistry of **1** also can be explained by a nearly coplanar π-system in the triplet. δ-Hydrogen abstraction gives a 1,5-biradical that must rotate so as to destroy benzylic conjugation in order for cyclization to an indanol to occur. This retarded rotation allows the biradical to undergo an otherwise less favorable reaction, namely a rearrangement to the unsaturated alcohol. In the benzophenone derivatives, the benzylic radical center of the biradical can remain conjugated with the unsubstituted benzene ring while the butylphenyl ring rotates.[1] In the *o-tert*-butylbenzophenones, hydrogen abstraction can take place even with a 70° twist so that the 1,5-biradical is formed almost in the correct geometry for cyclization.[3] We have corroborated Neckers' report that 2,4,6-tri-*tert*-butylacetophenone undergoes photocyclization to the indanol *tert*-butyl **6**.[13] The extra *tert*-butyl group apparently prevents even the triplet from attaining coplanarity such that it behaves like **2** instead of **1**.



We cannot yet assign a mechanism for the redox rearrangement; two major possibilities are disproportionation of a rearranged 1,5-biradical and a 1,5-sigmatropic hydrogen shift in a spiroenol. An unsaturated alcohol is a major photoproduct from *o*-isopropoxybenzophenone, so ditertiary 1,5-biradicals certainly can disproportionate appropriately.[14] A 1,2-aryl shift in the original 1,5-biradical, in competition with closure to indanol, would generate the biradical precursor to the major product. Such shifts have rate constants of only 10^2–10^3 s^{-1} in monoradicals,[15] so a more complicated process is required for the much shorter lived 1,5-biradical. As with the *o*-alkoxy ketones,[1] cyclization to a spiroenol is geometrically allowed in the original 1,5-biradical from **1**; and **3** gave evidence for ~1% of such a product.[3] We have not been able to trap such an intermediate from **1** with acetylene dicarboxylate. However, it would be expected to have a short lifetime because of a sigmatropic rearrangement to product or equilibration with the more stable of the two possible 1,5-biradicals. It is even possible that the biradical interconversion could proceed via a triplet spiroenol, just as the biradical formed by γ-hydrogen abstraction in *o*-alkyl ketones is a triplet enol.[16]

In summary, both the slow quenching of and the unusual products from an *o-tert*-butylacetophenone indicate that its triplet is much more coplanar than in the case of o-*tert*-butylbenzophenones. Therefore the 1,5-biradical formed by δ-hydrogen abstraction undergoes reactions dictated by a conjugatively restricted rotation.

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A Designed, Enantiomerically Pure, Fused Cyclopentadienyl Ligand with C_2 Symmetry: Synthesis and Use in Enantioselective Titanocene-Catalyzed Hydrogenations of Alkenes

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We report the synthesis of an enantiomerically pure, chiral cyclopentadienyl ligand[1,2] designed to possess C_2 symmetry and a rigid structural arrangement which effectively shields one face of an attached metal. Three X-ray structural analyses have served to establish relative and absolute configurations as well as structural features relevant to the interpretation of preliminary chemical data that strongly indicate synthetic utility.

The preparation of the key target **1** (generalizable for substituents other than phenyl)[3] is described in Scheme I.[4] It begins with *trans*-2-phenyl-4-cyclohexenol,[5] its stereoselective oxacyclopropanation,[6] and subsequent phenylcuprate ring-opening.[7] The resulting diol regiochemistry was established by ^{13}C NMR (7 lines, as expected for C_2 symmetry).

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(4) All new compounds gave satisfactory analytical and spectral data. For example, (+)-**1**: off-white crystals, mp (ethoxyethane) 188-189 °C; MS, *m/z* (rel intensity) 298.1720 (M^+, **2**, calcd for $C_{23}H_{22}$ 298.1723), 230 (100); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.76 (ddd, J = 15.4, 7.5, 3.0 Hz, 2 H), 2.49 (ddd, J = 15.4, 12.3, 3.6 Hz, 2 H), 2.88 (br s, 2 H), 3.04 (s, 2 H), 3.29 (ddd, J = 12.4, 7.5, 2.5 Hz, 2 H), 5.87 (s, 2 H), 7.17-7.35 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 37.3, 38.1, 41.2, 43.1, 121.5, 125.8, 127.8, 127.9, 146.9, 147.7; IR (KBr) 2974, 1509, 1465, 1410, 1266, 1044 cm^{-1}; $[\alpha]^{25}_D$ = +21.8° (*c* 1, methylbenzene). (+)-Cp_2*$TiCl_2$: yellow-brown crystals, mp (petroleum ether–CH_2Cl_2) 220–222 °C; MS, *m/z* (rel intensity) 679, 677 (M^+–Cl, 90 for ^{35}Cl isotope fragment), 642 (100); HRMS 677.2468, calcd for $C_{46}H_{42}ClTi$ 677.2454; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.12 (dd, J = 11, 8 Hz, 2 H), 2.15 (ddd, J = 20, 11, 3 Hz, 2 H), 2.36 (dd, J = 20, 8 Hz, 2 H), 2.49 (ddd, J = 11, 8, 3 Hz, 2 H), 3.23 (apparent t, "J" = 11 Hz, 4 H), 3.30 (apparent t, J = 8 Hz, 2 H), 3.90 2 H), 6.08 (dd, J = 4, 3 Hz, 2 H), 6.53 (m, 4 H), 7.05 (m, 16 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.3, 39.2, 39.4, 39.9, 41.8, 43.9, 107.8, 119.4, 123.7, 126.2, 126.6, 126.9, 127.5, 127.9, 128.6, 133.2, 142.8, 143.8, 153.2; IR (CH_2Cl_2) 3015, 2938, 2858, 1592, 1487, 1442, 1161, 1128, 1070, 1029, 969, 900 cm^{-1}; $[\alpha]^{25}_D$ = +381° (*c* 0.04, 1,2-dichloroethane).
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