The reported structure has the hydrogens well out of the plane of the ring.[9] If we place the hydrogens in the ring plane of the crystal structure, many internuclear distances are in better agreement with those found here. Another possibility is that librational motions in the dissolved molecule may yield slightly smaller effective distances. Of course, there can be some real difference between solution and crystal structures; the three rings in the crystal structure are not quite coplanar. A final source of discrepancies lies in the 2D NOE technique. Dilution experiments indicate that a very small amount of intermolecular dipolar interactions exist (estimated <10%) at the concentration used. Also, analysis of 2D NOE peak intensities needs refining.

The test case explored here justifies cautious use of 2D NOE for quantitative determination of several interproton distances. The combination of these distances and other geometric constraints (bond distances, bond angles, steric limitations) can be utilized with the distance geometry algorithm[12] to calculate a family of acceptable molecular structures (hopefully, closely related).

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Registry No. Proflavine, 92-62-6.

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Photocyclizations of *o*-(Benzyloxy)acetophenone and -benzophenone: Effects of Variable Rotational Freedom on Biradical Behavior

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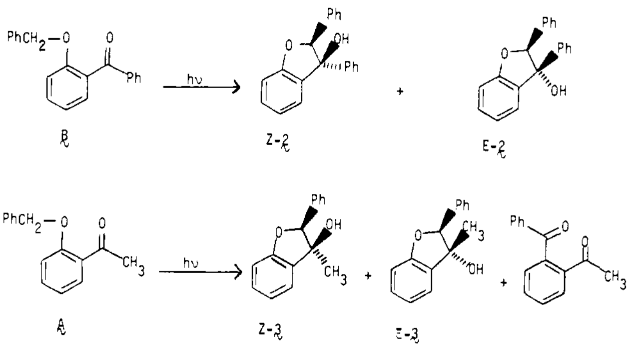
In all bimolecular photoreactions, acetophenone and benzophenone behave similarly.[1] Their n,π* triplets react with comparable rate constants, and they form the same kinds of products with comparable quantum efficiencies. We wish to report this similarity does not extend to intramolecular photoreactions, in particular the cyclization of *o*-(benzyloxy) ketones induced by triplet-state δ-hydrogen abstraction.[2] The benzophenone derivative reacts in a 50-fold greater quantum efficiency than the corresponding acetophenone, apparently because of much different rotational barriers and rates of intersystem crossing in the two 1,5-biradical intermediates.

o-(Benzyloxy)benzophenone (B), like some 4-alkoxy derivatives,[2c] cyclizes to the benzofuranols **2** upon UV irradiation. In benzene, the *Z/E* ratio is 8/1 and the combined quantum yield is 0.95. In the presence of Lewis base solvents, the product quantum yield falls to 0.60–0.65 and the *Z/E* ratio changes to 1.2:1. The reaction is readily quenched by typical triplet quenchers. Laser flash spectroscopy[3] revealed a transient triplet (λ_{max} = 540 nm) with a lifetime of 52 ns. No transient identifiable as a 1,5-biradical was apparent in benzene with enough diene to lower the triplet lifetime to <5 ns.[4] However, with added pyridine typical biradical decay (at 550 nm) could be observed with τ = 13 ns.



B Z-2 E-2

A Z-3 E-3

o-(Benzyloxy)acetophenone (A) also photocyclizes to benzofuranols, but in much lower quantum efficiency. In benzene, only (*Z*)-3 is detectable with Φ = 0.02. With 2 M pyridine present, the *Z/E* ratio is 1.5/1 while Φ = 0.20. In both solvent systems, 2-benzoylacetophenone is formed with Φ = 0.05–0.07. The rearrangements are readily quenchable in benzene. Flash spectroscopy reveals an identically quenchable triplet with a lifetime of 455 ns. This lifetime is too long to allow reliable detection of any substantially shorter lived biradical.

The remarkable observation that we must explain is the far greater efficiency with which the substituted benzophenone undergoes cyclization. Since the π,π* lowest triplet of A is less reactive than the n,π* lowest triplet of B,[5] A's low quantum yield could be partially due to radiationless decay competing with δ-hydrogen abstraction. However, the triplet lifetime ratio for A/B is the same as the ratio of rate constants for γ-hydrogen abstraction for valerophenone/*o*-methoxyvalerophenone, models for n,π* and π,π* triplets undergoing the same internal reaction.[6] Therefore δ-hydrogen abstraction is concluded to be the major mode of triplet decay for both A and B, and the lower quantum yields for A must involve competing reactions of the 1,5-biradical formed from the triplet.

Added Lewis bases destroy the stereoselectivity of cyclization for both ketones. This effect is well established for both 1,4-biradicals[7] and 1,5-biradicals,[2d,8] since the solvated OH is much larger than a free OH. Most hydroxy biradicals previously studied undergo a large amount of disproportionation back to starting ketone, which is suppressed by solvation of the OH.[7,8] The 10-fold enhancement of the cyclization quantum yield for A by added pyridine is thus typical behavior. What is unusual about A is the low overall quantum efficiency and the significant amount of diketone product.

The behavior of B is also unusual in that its biradical intermediate undergoes none of the usual disproportionation back to ground-state ketone. Solvation apparently impedes overall cyclization sufficiently that another process becomes competitive.[9] In fact, flash spectroscopy reveals a byproduct which has an absorption profile in the near-UV very similar to those of the LATs formed by para coupling of radicals during photoreduction of ketones.[10] Moreover, this byproduct is destroyed by addition of acid to the solution. We conclude that the biradicals also cyclize at the ortho position to form spiro enols. This competitive cyclization is minor with B but major with A. The benzoylaceto-

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(9) Previous investigators[2c,d] have correctly concluded that biradical solvation would slow down cyclization; we have shown that quantum yields are lowered only if another biradical process unaffected by solvation is competitive.[8]

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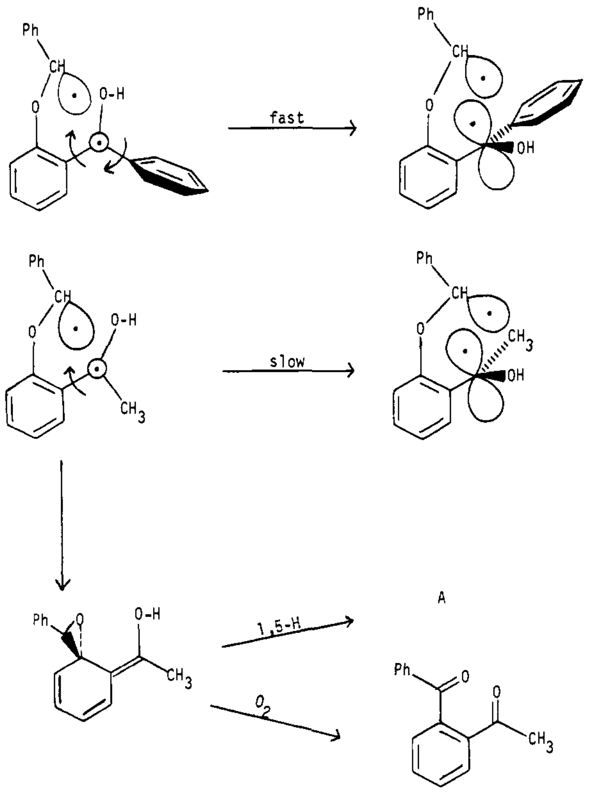
Scheme I



phenone formed from the latter is presumably an oxidation product of the spiro enol. We have not isolated any additional stable products in the case of B. However, the low yields of 4-alkoxy-2-hydroxybenzophenone formed from 4-alkoxy-B[2c] could well be due to oxidation of a spiro enol.

We conclude that A and B differ primarily in the relative rates of the competing biradical processes outlined in Scheme I. The efficiency of benzofuranol formation apparently is directly related to the ease of rotation about the aryl–C_1 bond. Inasmuch as the π-system of a substituted benzoyl group is conjugated in the triplet state, hydrogen abstraction produces a triplet 1,5-biradical with a fully conjugated benzyl radical center. A rotation of approximately 90° is required before cyclization can occur. In the acetophenone-derived biradical, such a rotation reduces the benzylic conjugation and thus is slow. In fact, an EPR study has provided a rate constant of only 10^3 s^{-1} for such a rotation in benzaldehyde ketyl radical.[11] This value may be too small for larger molecules, but the value would not exceed the 10^7 s^{-1} that has been established for rotation about the aryl–carbonyl bond of triplet ketones.[12] In contrast, rotation around one benzyl bond is facile in benzhydryl radicals because compensatory rotation about the other benzyl bond maintains benzylic conjugation. Therefore the B-derived biradical can rapidly rotate into the conformation necessary for cyclization to a furanol. As soon as the biradical becomes a singlet with the proper conformation, it can cyclize rapidly.

The competing spirocyclization does not require rotation about the benzyl bond. The biradical from A has more time than that from B to undergo this reaction, which thus predominates. The reaction could conceivably proceed adiabatically, forming the triplet state of the spiro trienol, although we have no evidence for this possibility. Oxidation of the spiro enol apparently competes with 1,5-sigmatropic hydrogen migration, which can regenerate starting ketone.

Ito, Matsuura, and co-workers have reported large quantum yields for benzocyclobutenol formation from *o*-isopropylbenzophenones[13] and have noted without explanation the very low values that we observed for the corresponding aryl alkyl ketones.[14] We propose that the same conjugative control of bond rotation in biradicals determines cyclization efficiency in both types of reaction. Ito and Matsuura also proposed the intriguing idea that rotation about the benzyl bond may induce the spin–orbit coupling required for intersystem crossing (isc) of the biradical intermediates.[13] This notion of rotation-induced isc has been popular for some time[15] but has not been clearly established as valid for any given system. That rotation may indeed be rate determining for cyclization of our 1,5-biradicals seems to follow from the unusually high efficiency with which B cyclizes. If rotational equilibrium were established before isc, disproportionation of the 1,5-biradical back to starting ketone should be significant.[8] Inasmuch as intersystem crossing determines triplet biradical lifetimes,[16] the very short lifetime for the unsolvated biradical formed from triplet B supports the idea of rotation-induced intersystem crossing.

The ether oxygen atoms make these 1,5-biradicals fully conjugated in the sense that there are p-orbitals on five adjacent atoms. Therefore rotation may have a larger effect on spin–orbit coupling than it does in nonconjugated biradicals. The lifetime-shortening effect of oxygen atoms in 1,4-biradicals may have a similar cause.[17] These ideas are being explored further wth differently substituted ketones.

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Registry No. (*Z*)-**2**, 93254-82-1; (*E*)-**2**, 93254-83-2; (*Z*)-**3**, 93254-84-3; (*E*)-**3**, 93254-85-4; A, 31165-67-0; B, 93254-81-0.

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Stereoselective Substituent Effects on Conrotatory Electrocyclic Reactions of Cyclobutenes

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When cyclobutenes undergo stereospecific conrotatory electrocyclic reactions to form butadienes,[2] substituents at C_3 or C_4 may rotate either "inward" or "outward" (Scheme I). We wish to report experimental results that establish that the energetic preference for substituents at C_3 and C_4 to rotate outward, rather than inward, increases as the π-donor nature of the substituent increases. Theoretical studies reveal a novel electronic origin of this phenomenon.[3]

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