Addition of Lithium Ester Enolates to Nitrobenzenes. Lithium enolates prepared from methyl propionate and γ-butyrolactone with LDA were reacted with nitrobenzene (−78 to 3 °C), 4-chloronitrobenzene (−20 °C, 2 h), 4-fluoronitrobenzene (−20 °C, 90 min), and 4-nitroanisole (−20 °C, 2 h), and the reaction mixtures were oxidized with bromine. No trace of coupling products were detected in any of these cases.

Registry No. **1a**, 31469-15-5; **1b**, 34880-70-1; **1c**, 51425-66-2; **1d**, 2916-76-9; **1e**, 6651-36-1; **1f**, 13735-81-4; **3**, 59115-08-1; **4**, 97522-00-4; **5b**, 30096-07-2; **5c**, 97522-01-5; **5d**, 30095-98-8; **5e**, 68614-38-0; **6b**, 50415-69-5; **6c**, 97522-02-6; **6d**, 2945-08-6; **6e**, 52648-78-9; **7b**, 92671-30-2; **7c**, 92671-31-3; **8a**, 92671-32-4; **8b**, 86790-37-6; **8c**, 92671-33-5; **8d**, 22908-29-8; **8e**, 92671-34-6; **8f**, 80805-54-5; **9b**, 92671-35-7; **9c**, 92671-36-8; **9f**, 97522-03-7; **10b**, 92671-37-9; **10e**, 97522-04-8; **11a**, 92671-38-0; **11e**, 97522-05-9; **12d**, 77158-65-7; **13b**, 97522-07-1; **14b**, 97522-08-2; **15**, 121-73-3; **15d**, 97522-09-3; **15e**, 97522-10-6; **16**, 86-57-7; **16a**, 97522-19-5; **16b**, 92671-40-4; **16c**, 92671-41-5; **17**, 581-89-5; **17b**, 97522-11-7; **17d**, 97522-12-8; **18**, 602-60-8; **19**, 6583-06-8; **19a**, 92671-42-6; **20**, 607-32-9; **20b**, 97522-13-9; **21**, 13599-78-5; **21a**, 97522-14-0; **21b**, 97522-15-1; **21d**, 97522-16-2; **22**, 609-40-5; **23**, 97522-17-3; **25**, 97522-18-4; **26**, 97522-20-8; **26** (1,4 isomer), 97522-21-9; **27**, 97522-22-0; **28**, 97522-23-1; **31**, 97522-24-2; **30**, 97522-26-4; **31**, 97522-25-3; **32a**, 97522-27-5; **32b**, 97522-28-6; **33**, 97522-29-7; **34**, 97522-30-0; **35a**, 14500-58-4; **35b**, 100-14-1; TASF, 59218-87-0; Bu_4NF, 429-41-4; nitrobenzene, 98-95-3; 1-chloro-4-nitrobenzene, 100-00-5; *m*-dinitrobenzene, 99-65-0; 1,3-dinitro-5-bromobenzene, 18242-39-2; *p*-nitroanisole, 100-17-4; methyl α-methyl-10-anthraceneacetate, 79938-37-7; 4-nitrocumene, 1817-47-6; cyclohexanone, 108-94-1; methyl propionate, 554-12-1; δ-butyrolactone, 96-48-0; 1-methyl-4-nitrobenzene, 99-99-0; 1-fluoro-4-nitrobenzene, 350-46-9; 1,3-dichloro-4-nitrobenzene, 611-06-3; 1-chloro-3-methoxy-4-nitrobenzene, 6627-53-8; 1-chloro-2-nitrobenzene, 88-73-3; 1-cyclopropyl-4-nitrobenzene, 6921-44-4; methyl 3-chloro-4-nitrobenzeneacetate, 97522-06-0; 1,2-dinitrobenzene, 528-29-0; methyl 3-nitrobenzeneacetate, 10268-12-9; 1,4-dinitrobenzene, 100-25-4.

Photocyclization of *o-tert*-Butylbenzophenone

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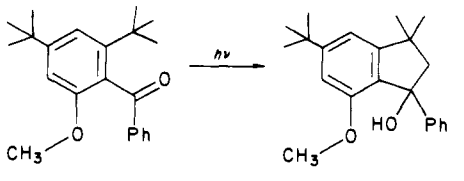
Abstract: UV irradiation of *o-tert*-butylbenzophenone as a solid or in solution from 77 K to room temperature results in its quantitative cyclization to 1-phenyl-3,3-dimethyl-1-indanol. The quantum efficiency is 0.04 in hydrocarbon solvents and 1 in methanol. Laser flash spectroscopy reveals the intermediacy of the expected 1,5-biradical, which has a lifetime in methanol of 43 ns from −100 to 25 °C but only 4 ns in toluene. This biradical is formed from a very reactive triplet, which has a lifetime greater than 10 ns only in alcohols below −70 °C. The variation of triplet lifetime with temperature (−70 to −130 °C) indicates an activation energy of 2.30 kcal/mol and an *A* factor of $10^{10.6}$ s^{-1} for δ-hydrogen abstraction by the triplet. Room temperature quenching of the cyclization indicates a rate constant $\geq 10^9$ M^{-1} s^{-1}. This exceptionally fast example of δ-hydrogen abstraction results from the ketone existing exclusively in a conformation ideal for internal hydrogen abstraction and may represent tunnelling. X-ray analysis of the crystal reveals that the *tert*-butylphenyl ring is twisted 69° from coplanarity with the carbonyl and that two of the *tert*-butyl hydrogens are within bonding distance of the oxygen. Oxygen and nitroxides increase the product quantum yield and decrease the biradical lifetime. This effect of paramagnetic additives is similar to that observed for 1,4-biradicals, but the solvent effect on biradical lifetimes is larger than usual.

The photochemistry of *o-tert*-butylphenyl ketones has been a subject of some confusion. Beckett and Porter originally reported that *o-tert*-butylbenzophenone (OTBBP) undergoes photodisappearance in 2-propanol and assumed that it was being photoreduced by solvent.[2] Neckers reported that 2,4,6-tri-*tert*-butylacetophenone photocyclizes inefficiently by presumedly slow δ-hydrogen abstraction.[3] O'Connell reported briefly that 2,4-di-*tert*-butyl-6-methoxybenzophenone photocyclizes to a 3,3-dimethyl-1-indanol derivative.[4] This report is striking because it suggests that *tert*-butyl primary hydrogens may be more reactive than methoxy hydrogens, when in fact anisole is known to be six times more reactive than *tert*-butylbenzene toward alkoxy radicals.[5] More recently, Bergmark and Kennedy reported that 2,5-di-*tert*-butylvalerophenone is stable to UV irradiation.[6] They ascribed this lack of reactivity to very rapid and totally reversible δ-hydrogen abstraction. These conclusions are unusual since δ-hydrogen abstraction normally is very slow.[7]



† Michigan State University.

Our combined interests in biradicals[8-12] and conformational effects on intramolecular reactions[13] prompted us to investigate the photobehavior of OTBBP as completely as possible. We report here our findings, which confirm all the earlier observations and most of the puzzling earlier conclusions, especially that of very rapid triplet δ-hydrogen abstraction, and reveal unusually large conformational and solvent effects on triplet hydrogen abstraction and on biradical decay.

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Results

Steady-State Photochemistry. Preparative scale irradition (313 or 300 nm) of deaerated benzene or methanol solutions of OTBBP (prepared by literature methods) at room temperature produced a single product, 3,3-dimethyl-1-phenyl-1-indanol, in a yield within experimental error of 100%. The quantum efficiency for degassed 0.02 M solutions irradiated to 2–3% conversion is 0.04 in benzene and 1.0 in methanol. Irradiation of small crystals of OTBBP on a glass plate also produced the indanol product quantitatively. The indanol dehydrates readily; the corresponding indene appears in variable amounts during GC analysis but is not present in irradiated samples analyzed only by NMR or HPLC.

The reaction can be quenched, albeit inefficiently. In hexane, with 1,3-pentadiene quencher, a linear Stern–Volmer plot was obtained with a slope of 2.3 ± 0.3 M^{-1}. In methanol, with ethyl sorbate quencher, the slope was 11 ± 1 M^{-1}. The quantum yield in benzene is doubled by 1.2 M methanol or when the reaction is carried out under oxygen rather than nitrogen atmosphere. Addition of 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) also produces increased cyclization quantum yields: 0.06, 0.07, and 0.09 for TEMPO concentrations of 0.009, 0.017, and 0.033 M, respectively. No new products were detected with TEMPO; with oxygen, GC–MS analysis revealed a new product apparently isomeric with OTBBP in only 3% yield with respect to indanol.

Excitation at −90 °C produces cyclization in quantum efficiencies comparable to those at room temperature. Even in an alcohol glass at 77 K there is some product formation, in a quantum efficiency estimated as 4%. UV spectra of irradiated methanol solutions reveal a byproduct which absorbs to the red of OTBBP, λ_{max} ca. 340 nm. There is much more of this byproduct formed at room temperature than at −90 °C. At 60% conversion, the optical density of this byproduct is comparable to that of initial ketone. If the absorption represents a π,π^* transition, the byproduct is formed in no more than 1% yield. Solutions containing this byproduct show intense fluorescence with maximum emission intensity at 422 nm.[14] The only significant products revealed by capillary GC–MS analysis of these solutions were the indanol and variable small percentages of the 1-phenylindene formed by dehydration. Low conversion irradiation of toluene solutions produced no 340-nm absorption; but high conversion gave some new absorption at ~320 nm. The fluorescent byproduct is also formed in toluene but in lower quantum efficiency than in alcohols.

Spectroscopy. OTBBP displays phosphorescence at 77 K very much like that of benzophenone itself with 0,0 bands at 408 and 405 nm in MCIP and a 9:1 ethanol:methanol mixture, respectively, a 1580 cm^{-1} 0,0–0,1 shift, and a lifetime of only 1.1 ms in both glasses. The emission of benzophenone in the latter glass is about five times more intense, with a 0,0 band at 413 nm and a 6 ms lifetime, as published.[15] OTBBP shows normal n,π^* absorption with a λ_{max} at 329 instead of 345 nm in hydrocarbon solvents.

Flash Kinetics. Solutions of OTBBP were prepared such that their optical densities in 7-mm square cells were ~0.6 at 337 nm or 0.2 at 308 nm, which conditions correspond to concentrations of 0.005 to 0.01 M. All solutions were deaerated by bubbling purified nitrogen through them for a few minutes. Most flash experiments were performed with a 308 nm excimer laser pulsing at 1 Hz (~80 mJ/4 ns pulse). At room temperature in benzene, transient decay was faster than or comparable with the laser pulse at all wavelengths monitored. In methanol, however, a transient with a 40-ns exponential decay was observed. This transient has a weak maximum at 465 nm, strong absorption below 330 nm, but no significant absorption above 600 nm (Figure 1). Addition of paraquat produced the characteristic absorption of the radical–cation at 600 nm.[16] Analysis of its growth kinetics as a function of paraquat concentration indicated a precursor lifetime

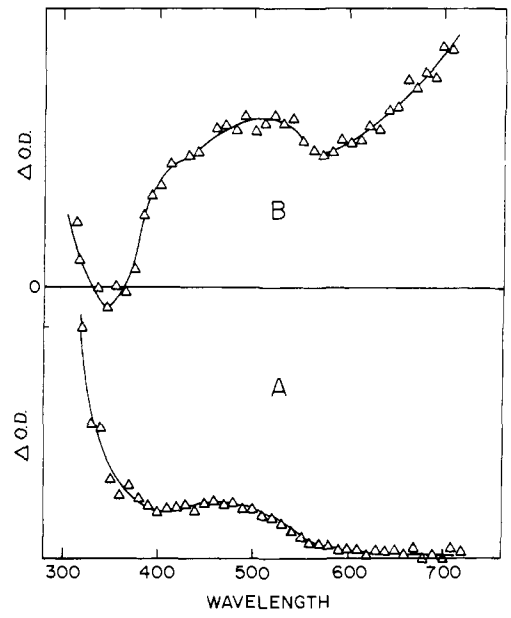

Figure 1. Transient absorption spectra obtained by pulsing ~0.005 M OTBBP in methanol at −90 °C with a 308-nm excimer laser. Spectrum A was measured 15–20 ns after each pulse and spectrum B, during the rise of the transient absorption, ~1 ns after the pulse. Maximum ΔOD was 0.038 in A and 0.031 in B.

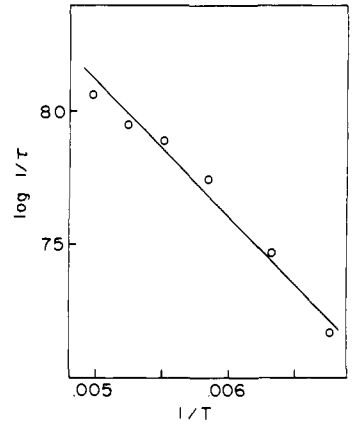

Figure 2. Arrhenius plot of transient decay rates measured at 620–650 nm following 308-nm pulsing of 9:1 ethanol:methanol solutions ~0.005 M in OTBBP.

of 40 ns and a bimolecular rate constant for electron transfer to paraquat of 9×10^8 M^{-1} s^{-1}. By analogy to many earlier studies,[11] these observations all indicate that the 40-ns transient is the 1,5-biradical expected from triplet-state δ-hydrogen abstraction.

At −90 °C in methanol, two transients could be observed. Monitoring at wavelengths below 390 nm revealed a 43-ns transient plus some longer-lived residual absorbance presumably due to the fluorescing byproduct mentioned above. (The relative amount of this residual was higher at higher temperatures.) Monitoring at wavelengths from 550 to 650 nm revealed a transient with a clean 10-ns exponential decay. Spectra obtained at short and long delays indicate that the 43-ns species is the same as the 40-ns species produced at room temperature. The 10-ns transient has a strong maximum at 525 nm and another maximum around 700 nm, with little absorption between 340 and 380 nm. The short lifetime of this species and the high solvent viscosity precluded identification by triplet quenching. However, the similarity of its spectrum (Figure 1) to that of some other substituted benzophenone triplets[17] allows us to assign it confidently as triplet OTBBP.

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(17) Benzophenone itself does not show strong absorption at 700 nm,[18] but we have found that several substiuted benzophenones do.

Table I. Positional Parameters and Standard Deviations in *o-tert*-Butylbenzophenone (MSU)[a]

atom	*X*	*Y*	*Z*	B_{EQ} (B_{ISO})
O(1)	0.3213 (2)	0.4487 (2)	0.0634 (2)	4.89
C(1)	0.2067 (4)	0.4940 (3)	0.2286 (3)	4.44
C(2)	0.1508 (4)	0.5096 (3)	0.3128 (3)	5.47
C(3)	0.0577 (4)	0.4697 (3)	0.3300 (3)	5.37
C(4)	0.0192 (4)	0.4139 (3)	0.2630 (3)	4.91
C(5)	0.0750 (3)	0.3976 (2)	0.1782 (3)	3.90
C(6)	0.1690 (3)	0.4375 (2)	0.1606 (2)	3.28
C(7)	0.2333 (3)	0.4210 (2)	0.0715 (3)	3.45
C(8)	0.1838 (3)	0.3737 (2)	−0.0117 (2)	2.98
C(9)	0.1052 (3)	0.4183 (2)	−0.0594 (3)	3.69
C(10)	0.0597 (3)	0.3889 (3)	−0.1434 (3)	4.42
C(11)	0.0906 (4)	0.3137 (3)	−0.1789 (3)	4.99
C(12)	0.1665 (4)	0.2684 (3)	−0.1314 (3)	4.64
C(13)	0.2160 (3)	0.2962 (2)	−0.0470 (2)	3.29
C(14)	0.3016 (3)	0.2431 (2)	0.0016 (3)	4.25
C(15)	0.2918 (5)	0.2427 (4)	0.1126 (4)	5.53
C(16)	0.4092 (4)	0.2779 (4)	−0.0282 (4)	6.16
C(17)	0.2964 (6)	0.1514 (3)	−0.0325 (5)	7.25
H(1)	0.273 (2)	0.518 (2)	0.214 (2)	4.3 (9)
H(2)	0.181 (3)	0.549 (2)	0.357 (3)	6.4 (11)
H(3)	0.017 (3)	0.484 (2)	0.393 (3)	5.8 (10)
H(4)	−0.048 (3)	0.386 (2)	0.276 (3)	7.6 (13)
H(5)	0.049 (2)	0.356 (2)	0.131 (2)	4.0 (9)
H(9)	0.083 (2)	0.473 (2)	−0.032 (2)	4.0 (8)
H(10)	0.004 (2)	0.422 (2)	−0.174 (2)	4.7 (9)
H(11)	0.061 (3)	0.289 (2)	−0.241 (3)	5.3 (10)
H(12)	0.180 (2)	0.214 (2)	−0.158 (2)	3.5 (8)
H(15A)	0.219 (3)	0.222 (3)	0.133 (3)	8.9 (15)
H(15B)	0.306 (3)	0.297 (2)	0.142 (3)	6.1 (12)
H(15C)	0.346 (4)	0.203 (3)	0.145 (3)	11.2 (16)
H(16A)	0.435 (4)	0.341 (3)	−0.009 (4)	12.3 (19)
H(16B)	0.420 (3)	0.280 (2)	−0.099 (3)	5.9 (12)
H(16C)	0.464 (3)	0.242 (2)	−0.002 (2)	5.2 (10)
H(17A)	0.316 (3)	0.152 (2)	−0.108 (3)	8.3 (14)
H(17B)	0.220 (3)	0.130 (3)	−0.013 (3)	7.3 (14)
H(17C)	0.353 (4)	0.119 (3)	0.007 (3)	9.8 (15)

[a] Calculated standard deviations are indicated in parentheses.

The lifetime of this triplet transient, monitored at 620 and 650 nm, was measured in a 9:1 ethanol:methanol mixture from −133 to −70 °C. Figure 2 shows the Arrhenius plot for the data, which indicates E_a = 2.30 ± 0.34 kcal/mol and log (A/s^{-1}) = 10.6 ± 0.43. The lifetime of the biradical transient, monitored at 330–480 nm, was measured as 43 ± 3 ns in methanol at several temperatures from −90 to 26 °C.

In toluene at −90 °C, monitoring at 480–650 nm reveals an 8.5 ± 0.5 ns triplet. As in methanol, its spectrum has maxima at 535 and 700 nm. The biradical is much shorter lived and therefore harder to detect in toluene or benzene than in alcohols. In toluene at room temperature, the transient signal at 330 nm decays with a lifetime only slightly longer than the duration of the laser pulse. Deconvolution[19] indicates a lifetime of 4.2 ns. The spectrum of the biradical agrees well with that recorded in methanol.

The difficulty of observing triplet ketone and biradical in hydrocarbon solvents might have been due to low triplet yields. Benzene solutions containing OTBBP and 0.01–0.2 M 1-methylnaphthalene were flashed at room temperature with the 337-nm laser. A double reciprocal plot of sensitized triplet naphthalene formation[20] displayed an intercept of 0.85 and a $k_q\tau$ value (intercept/slope) of 3.4 M^{-1}. Correction for direct competing absorption by the naphthalene indicates an intersystem crossing yield within experimental error of unity.

Biradical lifetimes varied with solvent polarity as follows: 32 ns in 50% aqueous dioxane; 24 ns in *tert*-butyl alcohol; 20 ns in diethyl ether or acetonitrile containing 10% water; <6 ns in Freon-113. The values in benzene containing 20% and 5% methanol (by volume) were 12 and 8 ns, respectively. These lifetimes were shortened significantly when the solutions were saturated with oxygen. The values measured were 25 ns in a 1:1 water:dioxane moisture, 11 ns in methanol, and <8 ns in less polar solvents. The lifetime shortening effected by 10^{-2} M oxygen in

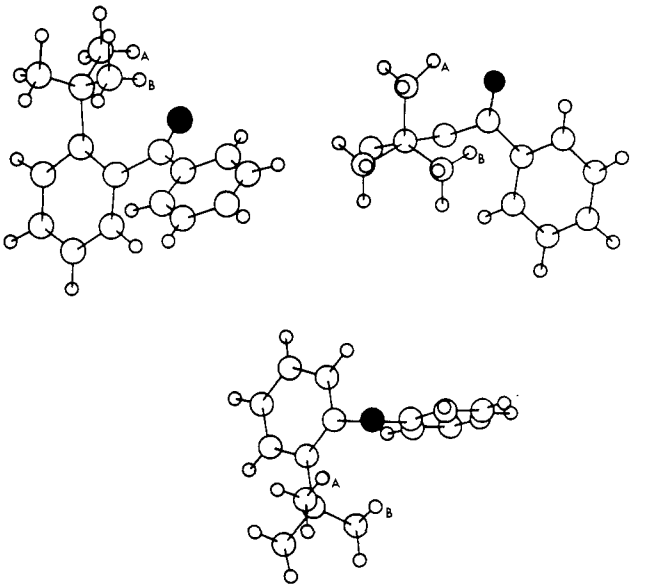

Figure 3. Three perspectives of molecular OTBB as determined from its crystal structure. The dark represents oxygen. Some of the ring hydrogens have been left out for the sake of clarity. Hydrogens A and B in the text are so labeled.

Table II. Interatomic Distances and Standard Deviations in *o-tert*-Butylbenzophenone (MSU)

atoms		distance, Å
C(7)	O(1)	1.214 ± 0.004
C(2)	C(1)	1.380 ± 0.006
C(6)	C(1)	1.388 ± 0.005
C(3)	C(2)	1.371 ± 0.006
C(4)	C(3)	1.375 ± 0.006
C(5)	C(4)	1.389 ± 0.005
C(6)	C(5)	1.383 ± 0.005
C(7)	C(6)	1.493 ± 0.004
C(8)	C(7)	1.510 ± 0.004
C(9)	C(8)	1.395 ± 0.005
C(13)	C(8)	1.399 ± 0.004
C(10)	C(9)	1.374 ± 0.005
C(11)	C(10)	1.363 ± 0.005
C(12)	C(11)	1.377 ± 0.005
C(13)	C(12)	1.392 ± 0.005
C(14)	C(13)	1.540 ± 0.005
C(15)	C(14)	1.527 ± 0.006
C(16)	C(14)	1.539 ± 0.006
C(17)	C(14)	1.548 ± 0.006
H(1)	C(1)	0.951 ± 0.030
H(2)	C(2)	0.955 ± 0.037
H(3)	C(3)	1.035 ± 0.035
H(4)	C(4)	0.987 ± 0.038
H(5)	C(5)	0.984 ± 0.030
H(9)	C(9)	0.998 ± 0.029
H(10)	C(10)	0.988 ± 0.032
H(11)	C(11)	1.004 ± 0.033
H(12)	C(12)	0.965 ± 0.029
H(15A)	C(15)	1.025 ± 0.041
H(15B)	C(15)	0.979 ± 0.035
H(15C)	C(15)	1.045 ± 0.049
H(16A)	C(16)	1.094 ± 0.048
H(16B)	C(16)	0.980 ± 0.035
H(16C)	C(16)	0.976 ± 0.035
H(17A)	C(17)	1.067 ± 0.038
H(17B)	C(17)	1.062 ± 0.038
H(17C)	C(17)	1.043 ± 0.047

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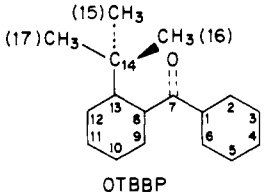
Table III. Interatomic Angles and Standard Deviations in *o-tert*-Butylbenzophenone (MSU)

atom 1	atom 2	atom 3	angle, deg
C(2)	C(1)	C(6)	120.09 ± 0.47
C(1)	C(2)	C(3)	120.48 ± 0.43
C(2)	C(3)	C(4)	120.03 ± 0.45
C(3)	C(4)	C(5)	119.96 ± 0.48
C(4)	C(5)	C(6)	120.23 ± 0.45
C(1)	C(6)	C(5)	119.21 ± 0.39
C(1)	C(6)	C(7)	118.32 ± 0.38
C(5)	C(6)	C(7)	122.46 ± 0.37
O(1)	C(7)	C(6)	121.21 ± 0.29
O(1)	C(7)	C(8)	120.24 ± 0.29
C(6)	C(7)	C(8)	118.43 ± 0.31
C(7)	C(8)	C(9)	113.35 ± 0.33
C(7)	C(8)	C(13)	125.88 ± 0.31
C(9)	C(8)	C(13)	120.53 ± 0.37
C(8)	C(9)	C(10)	121.29 ± 0.36
C(9)	C(10)	C(11)	118.88 ± 0.40
C(10)	C(11)	C(12)	120.30 ± 0.42
C(11)	C(12)	C(13)	122.87 ± 0.42
C(8)	C(13)	C(12)	116.11 ± 0.34
C(8)	C(13)	C(14)	123.66 ± 0.31
C(12)	C(13)	C(14)	120.23 ± 0.37
C(13)	C(14)	C(15)	112.03 ± 0.34
C(13)	C(14)	C(16)	108.45 ± 0.34
C(13)	C(14)	C(17)	111.58 ± 0.37
C(15)	C(14)	C(16)	109.89 ± 0.47
C(15)	C(14)	C(17)	107.09 ± 0.43
C(16)	C(14)	C(17)	107.71 ± 0.45

methanol corresponds to a rate constant of 7×10^9 M^{-1} s^{-1}.

X-ray structure analysis was performed both at Michigan State and at the NRC, with essentially identical results. In all subsequent discussion, results from MSU are used unless otherwise stated. OTBBP crystallized from heptane as colorless, transparent orthorhombic crystals: space group *Pbca*; a = 12.770 (2) Å, b = 16.082 (4) Å, c = 13.706 (3) Å at MSU; at NRC, a = 12.781 (1) Å, b = 16.096 (2) Å, c 13.703 (1); Å; Z = 8; M = 238.33; ρ_c = 1.125 g cm^{-3}. Figure 3 presents several computer generated perspectives of the molecular structure. Table I lists all positional parameters measured at MSU while Tables II and III list key bond lengths and angles. Other crystallographic data and all NRC results are inluded in supplementary material.

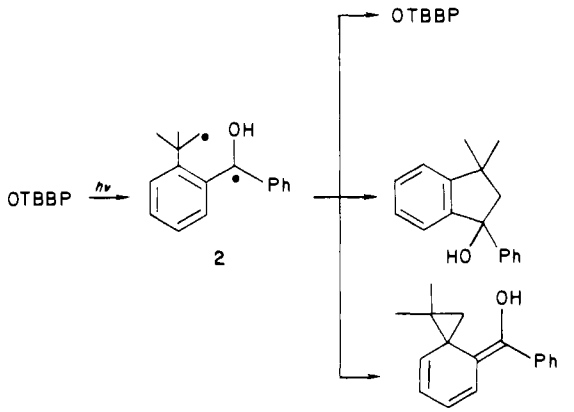
OTBBP has a few bond lengths slightly longer than those in benzophenone, and the C–H bond of the hydrogen closest to the carbonyl is 1.09 ± 0.05 Å long. The major accommodation which the molecule makes to the bulk of the *tert*-butyl group is a change in bond angles at the two carbons bearing the benzoyl and *tert*-butyl groups. The angles 7,8,13 and 8,13,14 are opened up to 126° and 124°, the former representing a tilt of the benzoyl substituent and the latter representing a distortion of the benzene ring.



OTBBP

Discussion

As suggested by earlier reports,[3,4] OTBBP undergoes triplet-state δ-hydrogen abstraction to generate the 1,5-biradical **2**. This particular 1,5-biradical can undergo only three chemical reactions: disproportionation back to ground-state ketone; cyclization to the indanol; and spirocyclization to a trienol. In hydrocarbon solvents, disproportionation predominates. In methanol, only cyclization occurs. In both cases the *chemical* yield of indanol is within experimental error of 100%. The indanol is easily dehydrated to a 1-phenylindene, but this secondary product is not responsible for the transient absorbing at 340 nm in methanol. We presume that this absorption represents ~1% spirocyclization, since the trienol para-coupling products of hemipinacol radicals absorb in this region.[21] The same reaction apparently occurs even less efficiently in aromatic solvents. Previously studied 1,5-biradicals which can disproportionate to the enol form of starting ketone do so efficiently independent of solvent,[22,23] but such is not possible here.



The quantitative aspects of these results provide several points of interest: (1) the unusually high reactivity of triplet OTBBP in solution, even at low temperatures; (2) the reactivity in the crystalline state; (3) the solvent effects on triplet reactivity; (4) the large solvent effect on biradical lifetime and cyclization efficiency; and (5) an explanation of earlier results. All these points require proper consideration of the molecule's geometry.

Molecular Geometry. It is well known that ground-state benzophenone has a propellar shape, with each ring being twisted some 30°.[24] The UV and IR spectra of OTBBP both suggest that the carbonyl is less conjugated than in benzophenone itself. Interestingly, the ^{13}C carbonyl chemical shift (200.16) is only slightly higher than those for *o*-methylbenzophenone (198.5) and benzophenone itself (196.48).[25] Therefore, we conjectured that the ground state of OTBBP exists primarily in a conformation with the *tert*-butylphenyl ring twisted almost totally out of conjugation with the carbonyl, in agreement with the lack of internal hydrogen bonding noted for 2-hydroxy-4,6-di-*tert*-butylbenzophenone.[26] As the X-ray derived structures in Figure 3 reveal, the *tert*-butylphenyl ring is indeed twisted 69° out of conjugation with the carbonyl. The phenyl ring is twisted only 11°. As expected,[27] the *tert*-butyl group is closer to the carbonyl oxygen than to the benzene ring, such that one of the *tert*-butyl hydrogens (H_A) is held some 2.2–2.4 Å from the carbonyl oxygen and 40° above the nodal plane of the carbonyl π system. Another (H_B) is held 2.7 Å from the oxygen and perpendicular to the same nodal plane. We presume that the molecule has a similar shape in solution. Inspection of the molecular model indicates that at least one *tert*-butyl hydrogen atom stays within 2.7 Å of the carbonyl oxygen even at a 90° twist between the carbonyl group and the *tert*-butylphenyl ring.

The molecule probably has very little conformational freedom. The *tert*-butyl group undergoes relatively facile rotation in solution, since its NMR signal remains a sharp singlet down to −90 °C. The conformation in the crystal must be that of minimum internal energy, since the crystal lattice cannot distinguish among various rotations of the symmetric *tert*-butyl group. Rotation around the butylphenyl–carbonyl bond presumably is quite limited because of combined steric and conjugative effects.

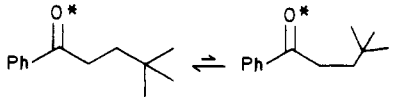
The slightly higher energy phosphorescence of OTBBP relative to benzophenone suggests that the *tert*-butyl group decreases overall conjugation in the triplet. It is believed that triplet ben-

(21) Filipescu, N.; Minn, F. L. *J. Am. Chem. Soc.* **1968**, *90*, 1544.
(22) Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.* **1979**, *101*, 7134.
(23) Wagner, P. J.; Meador, M. A. *J. Am. Chem. Soc.* **1984**, *106*, 3684.
(24) Fleischer, E. B.; Sung, N.; Hawkinson, S. *J. Phys. Chem.* **1968**, *72*, 4311.
(25) For a discussion of ortho substituent effects on conjugation and ^{13}C chemical shifts, see: Leibfritz, D. *Chem. Ber.* **1975**, *108*, 3014.
(26) Shulgin, A. T.; Kerlinger, H. O. *Chem. Commun.* **1966**, 249.
(27) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* **1976**, *98*, 239.

zophenone exists with one nearly planar benzoyl group and the other benzene ring twisted even more than in the ground state.[28] Consequently, triplet OTBBP probably exists in only one significant conformation not much different from that of the ground-state crystal, with the *tert*-butylphenyl group twisted nearly out of conjugation with the carbonyl but with at least one primary hydrogen atom always within bonding distance of the carbonyl oxygen. The major difference between ground and excited states probably is a longer C–O bond in the excited state.[29]

Triplet Reactivity. The high intersystem crossing yield indicates that singlet reactivity is not so high as to compete significantly with the rapid intersystem crossing of benzophenone. δ-Hydrogen abstraction by triplet OTBBP obviously is very rapid. The Arrhenius parameters measured between 140 and 200 K provide extrapolated rate constants of 10^4 s^{-1} at 77 °C and 8×10^8 s^{-1} at 25 °C in alcohol solvent. These extrapolations appear to be fairly accurate. We measured a 1-ms lifetime at 77 K and observed reduced phosphorescence as well as product formation; so hydrogen abstraction must be competitive with phosphorescence. The values of k_q for quenching of unhindered phenyl ketone triplets at room temperature are 1.3×10^{10} and 0.9×10^{10} M^{-1} s^{-1} for dienes in hexane and methanol and 8×10^9 for naphthalene in benzene.[30,31] Therefore, the quenching and sensitization results indicate maximum values for $k_{\delta\text{-H}}$ of 5×10^9 s^{-1} in hexane, 2.3×10^9 s^{-1} in benzene, and $\sim 1 \times 10^9$ s^{-1} in methanol, values close to those extrapolated from lower temperatures. We have observed some steric hindrance to energy transfer for other-substituted ketones,[32] so it is possible that the actual high-temperature rates are slightly slower. The activation energy in aromatic solvents appears to be comparable to that in alcohol, based on only two temperature points.

The unusually large value of $k_{\delta\text{-H}}$ for OTBBP must reflect the limited number of conformations available to the molecule. In contrast, γ,γ-dimethylvalerophenone (**3**), the analogous acyclic compound, undergoes triplet-state δ-hydrogen abstraction with a rate constant of only 3×10^5 s^{-1}.[7] The two β-*tert*-butyl ketones differ in reactivity by four orders of magnitude! Lewis has shown[33] that rate constants for γ-hydrogen abstraction increase by roughly one order of magnitude for every frozen bond rotation, as predicted from basic kinetics considerations.[34] The effect here is far larger than might have been anticipated for the loss of a single free rotation in going from **3** to OTBBP.



3

Arrhenius parameters have been measured for other triplet-state hydrogen abstractions; an E_a value of 5.8 kcal/mol and an A factor of 10^{11} s^{-1} are reported for butyrophenone,[34,35] which has unactivated primary hydrogens just as in OTBBP. Lewis' work[33] indicates that E_a is constant and A increases as ketones with secondary γ-hydrogens become more inflexible. Therefore, we rather expected to find E_a and A values of 5–6 kcal/mol and $\geq 10^{12}$ s^{-1}, respectively. The lower values which we have measured and which appear to be valid over an extremely wide temperature range do not appear to fit a simple hydrogen atom abstraction process.

Before getting the crystal structure, we speculated that the activation parameters might measure rate-determining rotation around the *tert*-butylphenyl–carbonyl bond. Various considerations make this possibility unlikely, particularly the linear Arrhenius behavior over such a wide temperature range. The expected activation parameters would predict an intrinsic rate constant $\leq 10^9$ s^{-1} for hydrogen abstraction at 300 K, such that k_H might just compete with k_{rot}.[13] However, the same parameters predict rates much lower than observed at low temperatures. The crystal structure shows that there is no need to invoke a rate-determining rotation; a hydrogen is within bonding distance[36] of the carbonyl oxygen for all twist angles of the *tert*-butylphenyl ring with respect to the carbonyl, from 0 to 90°. The only way that rotation could be rate determining would be for triplet OTBBP to exist primarily in a twisted anti conformation. This possibility seems unlikely given the crystal structure and the established fact that the percentage of anti rotamer decreases as the ortho substituent gets larger.[25] The intensities of the temperature-dependent triplet transients were too strong to represent light absorption by only a small fraction of the ketone molecules. Moreover, there was no evidence either in quenching or flash studies for the presence of more than one triplet.

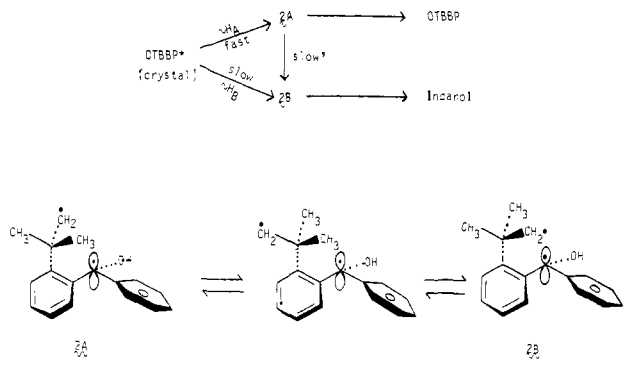
If we eliminate a rotational process as well as a normal activated hydrogen abstraction, we are left with tunnelling as an explanation for the low activation parameters. There is good evidence for tunnelling in some thermal and at least one excited-state hydrogen transfer.[37] We prefer to wait for additional evidence before discussing tunnelling more fully. In this regard, the solvent effect on triplet reactivity warrants mention. The reaction appears to be several times faster in hydrocarbon solvents than in methanol. Such solvent effects normally occur only when the electronic nature of the lowest triplet is altered.[38] Since simply substituted benzophenones maintain n,π* lowest triplets in all solvents, either an unusual form of reactivity is present or there is an unusual solvent effect on conformation. Given the previously discussed structural peculiarities of OTBBP, we see no obvious way for solvation-promoted conformational change to hinder hydrogen abstraction.

Comparison with Previous Results. The unexpectedly high reactivity of triplet OTBBP is responsible for the confusion about the meaning of earlier reports. Thus the quantum yield of 0.5 for disappearance of OTBBP in propanol[2] represents internal cyclization rather than photoreduction by solvent, since the latter has a pseudounimolecular rate constant of only 10^7 s^{-1} for benzophenone itself.[17,39] O'Connell's result[4] could have been due to different cyclization efficiencies of competitively formed 1,5-biradicals but obviously does reflect the high reactivity of an *o-tert*-butyl group as well as the conformationally depressed reactivity of an *o*-alkoxy group.[40] Finally, Bergmark's speculation that the reactivity of an *o-tert*-butyl group is high enough to dominate over γ-hydrogen abstraction was right on the mark.[6] We are now investigating the cause of the low cyclization efficiency in other *o-tert*-butyl ketones.[3,6]

Reactivity of Solid OTBBP. Intramolecular hydrogen abstraction by excited ketones in the solid state generally is confined to cyclic systems with little or no rotational freedom.[36] The steric congestion of OTBBP reduces its rotational freedom; the molecule assumes a geometry in the crystal lattice with the hydrogen atom H_A only 2.2–2.4 Å distant from the carbonyl oxygen and 40° above the nodal plane of the carbonyl π-system. Scheffer's elegant work on solid-state photochemistry has shown that triplet-state hydrogen abstraction is quite facile for such geometries.[36] In particular, γ-hydrogen abstraction occurs in solid α-cyclohexylacetophenones with an O–H distance of 2.6 Å and a dihedral angle of 42°.[41] In

(28) Hoffmann, R.; Swenson, J. R. *J. Phys. Chem.* **1970**, *64*, 415.
(29) Chandler, W. D.; Goodman, L. *J. Mol. Spectrosc.* **1970**, *35*, 232.
(30) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.
(31) Leigh, W.; Scaiano, J. C., unpublished work.
(32) Scaiano, J. C.; Leigh, W.; Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.*, in press.
(33) Lewis, F. D.; Johnson, R. W.; Kory, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 6100.
(34) Grotewold, J.; Soria, D.; Previtali, C. M.; Scaiano, J. C. *J. Photochem.* **1972/1973**, *1*, 471.
(35) Encinas, M. V.; Lissi, E. A.; Lemp, E.; Zanocco, A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 1856.
(36) Scheffer, J. R.; Dzakpasu, A. A. *J. Chem. Soc.* **1978**, *100*, 2163.
(37) (a) Grellmann, K.-H.; Weller, H.; Tauer, E. *Chem. Phys. Lett.* **1983**, *95*, 195. (b) Colpa, J. P.; Press, B.; Stehlik, D. *Chem. Phys. Lett.* **1984**, *107*, 469.
(38) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.
(39) Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2038.
(40) Wagner, P. J.; Meador, M. A.; Giri, B. P.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1087.
(41) Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1983**, *105*, 6959.

Scheme I



OTBBP, H_A is held at a 30° angle (away from the carbonyl carbon) from a line through the oxygen and perpendicular to both the carbonyl π-plane and the C–O bond. Scheffer has pointed out that if this angle were too large, the hydrogen would not overlap sufficiently with the oxygen n orbital.[36] All of his examples had such angles near 0° *in the ground state*, so there is no experimental indication of how much a bend is too much. We should point out that the well-known elongation of the excited C–O bond[29] would make the angle close to 0 in OTBBP.

Another *tert*-butyl hydrogen atom, H_B, lies 2.7 Å from the carbonyl oxygen and directly above the carbonyl carbon, almost perpendicular to the oxygen n orbital. That distance is barely within reaction range.[36] However, the simplest theories of excited-state reactivity[42] plus some experimental examples[43] suggest negligible hydrogen abstraction reactivity for n,π^* triplets such orientations. We do not, however, dismiss this "forbidden" process from being at least partially responsible for the solid-state photocyclization. We presume that the most favored triplet reaction is abstraction of H_A. The change in structure upon proceeding from ketone to biradical **2** is undoubtedly slight. We do not know whether **2A**, formed by attack on H_A, can undergo the bond rotation necessary for cyclization *in the crystal lattice*.[44] There is one example of a photogenerated biradical which has enough freedom to rotate and form product in the crystal[41] and one example of one which cannot.[45] Therefore, it is possible that the less favored abstraction of H_B competes to a small degree and that the resulting biradical **2B** cyclizes very efficiently, since it has a geometry very close to that required for cyclization. This mechanistic scenario is portrayed in Scheme I. It is also possible that all photoreaction takes place at the surface and at crystal defects, where molecular rotation is more facile than in the bulk crystal.[46] We trust that eventual measurements of solid-state quantum efficiencies will provide better answers.

Solvent Effects and Quantum Efficiencies. It is interesting to compare the behavior of biradical **2** with that of typical 1,4- and 1,5-biradicals generated by triplet-state γ- or δ-hydrogen abstraction. In nonbasic solvents, disproportionation is favored 24:1 over cyclization and spirocyclization is very inefficient. When the biradical's hydroxyl group is hydrogen bonded in methanol, disproportionation *at OH* is totally suppressed, as in most other biradicals.[8,22] Although the efficiency of normal cyclization now comes within experimental error of 100%, the appearance of some spiroenol indicates that the relative rate of cyclization by the product-forming biradical is slowed somewhat, as it is in all solvated hydroxybiradicals,[8,22] or that the rate of spirocyclization is increased. The latter seems very unlikely. It is worth noting that the steric crowding around the OH in **2** has the usual[47] effect of causing large concentrations of methanol to be needed to enhance product formation.

The lifetime of **2** is independent of temperature over a large range in alcohol solvent, but is 10 times longer in alcohol than in hydrocarbon. This behavior and the solvent effects in general are qualitatively the same as those for many 1,4-biradicals.[48] The difference is that this 1,5-biradical is distinctly shorter lived than most type II 1,4-biradicals and shows a larger solvent effect. Typical 1,4-biradicals have lifetimes of 30 and 100 ns in benzene and methanol, respectively.[10]

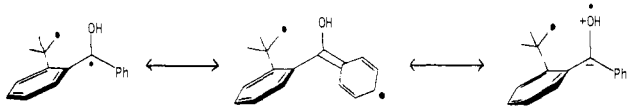
There is a good deal of independent evidence[10,49] that intersystem crossing (isc) is the rate-determining step in triplet biradical decay, perhaps the most compelling of which is the temperature independence and low preexponential factors for 1,4-biradical decay. 1,5-Biradical **2** is no exception in this regard. Furthermore, **2** interacts with oxygen and TEMPO so as to cyclize more efficiently. This effect of paramagnetic additives has been attributed to assisted intersystem crossing.[10,50–52] The fact that 0.01 M oxygen and 0.03 M TEMPO have the same effect on quantum yields as 1.2 M methanol makes a hydrogen-bonding explanation for the paramagnetic additives quite unlikely. On the other hand, the effects of solvent and structural changes on biradical lifetimes have not been easy to explain. Most attempts have been based on the assumption that rate-determining isc is faster the closer the two radical centers are to each other.[10,53] Unfortunately, the behavior of **2** is difficult to fit with the conformation-dependent isc model.

As pointed out earlier,[10,51] an enhancement of intersystem crossing rate by a paramagnetic additive cannot of itself explain a change in product partitioning. For the 1,4-biradicals generated by Norrish type II reactions, one of us has proposed that paramagnetic additives modify the conformations from which intersystem crossing occurs and that the singlet biradicals maintain their conformational memory.[10] If we assume that the major conformational freedom in **2** involves rotation of the *tert*-butyl group, there are then three major, nearly degenerate rotamers, as indicated in Scheme I. Spontaneous isc in **2B** and **2A** would lead preferentially to cyclization or back reaction, respectively. In essence the singlet biradicals would behave much like the two different rotamers frozen in a crystal lattice suggested in Scheme I. The third rotamer must rotate to one of the others to react chemically. Assisted isc of this conformer, which has the greatest distance between radical centers, would produce a singlet biradical which gives by rotation 50% of each reactive conformer. In fact, extrapolation of the TEMPO product enhancement results to infinite TEMPO concentration[51,52] indicates that only $^1/_3$–$^1/_2$ of the TEMPO–biradical interactions lead to indanol. Biradical **2** thus fits the model, but only if the "cyclization" geometry undergoes spontaneous isc more slowly than the "back-transfer" geometry, despite the larger distance between radical centers in the latter.

Inasmuch as distance between radical centers is important in controlling isc rates, one would expect a 1,5-biradical to live longer than a 1,4-biradical, especially if through bond interactions are important in the latter.[54] One might propose that conjugation of the benzyl radical center of **2** with the internal benzene ring brings the spins closer together than in type II 1,4-biradicals. However, what with the 69° twist of the *tert*-butylphenyl ring and the benzyl radical center being fully conjugated with the OH and with the other benzene ring, there cannot be even 1% spin density

(42) (a) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41. (b) Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486.
(43) (a) Sugiyama, N.; Nishio, T.; Yamada, K.; Aoyama, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1879. (b) Colpa, J. P.; Stehlik, D. *Chem. Phys.* **1983**, *81*, 163.
(44) Appel, W. K.; Jiang, Z. Q.; Scheffer, J. R.; Walsh, L. *J. Am. Chem. Soc.* **1983**, *105*, 5354.
(45) Quinkert, G.; Tabata, T.; Hickman, E. A. J.; Dobrat, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 198.
(46) Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386.
(47) Wagner, P. J.; Kochevar, I.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.
(48) Unfortunately, δ-hydrogen abstraction in most acyclic ketones is too slow to allow direct observation of the resulting 1,5-biradicals.
(49) Caldwell, R. A.; Sakuragi, H.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 2471.
(50) Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4512.
(51) Encinas, M. V.; Scaiano, J. C. *J. Photochem.* **1979**, *11*, 241.
(52) Scaiano, J. C.; Lee, C. W.; Chow, Y. L. *J. Phys. Chem.* **1982**, *86*, 2452.
(53) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629.
(54) Hoffman, R.; Swaminathau, S.; Odell, B. G.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 7081.

at the carbon bearing the butyl group. Moreover, if such a small fraction of 1,3-biradical character could control isc rates, paramagnetic quenchers could not distinguish among conformations. It is possible that the restricted geometry of **2** might keep the two radical centers closer on average than in a typical type II 1,4-biradical, as proposed for the biradical formed from *cis*-2-ethyl-1-benzoylcyclopropane.[10] However, Caldwell has just reported evidence against this possibility for two other 1,4-biradicals.[55]



One of us has proposed that solvent effects on biradical lifetimes reflect differential stabilization of different conformations and thus of different distances between free spins.[10] Application of this line of reasoning to these results would compel us to conclude that solvation by methanol substantially increases the distance between the two radical centers in our 1,5-biradical. Inspection of the molecule's structure suggests no obvious way for this to occur. Biradical **2**, like its precursor ketone, has very little conformational freedom. Solvation makes the OH more nearly as large as the phenyl[8] and thus would encourage the biradical to adopt a geometry with the *tert*-butylphenyl ring more nearly perpendicular to the C–O bond. This change would bring the alkyl radical center closer to, not farther from, the ketyl radical center. Apart from these specific structural considerations, it is hard to understand a biradical with almost no conformational freedom showing a larger solvent effect on conformationally determined intersystem crossing than those with considerable conformational freedom.

It has been pointed out that biradicals formed from triplet benzophenones may undergo particularly rapid intersystem crossing because of free rotation around the aryl–C(OH) bond.[56] The short lifetime of unsolvated biradical **2** certainly indicates rapid intersystem crossing. If the singlet biradical were to achieve conformational equilibrium before reacting, the solvent effect on quantum yields would indicate that the rate of decay of the unsolvated biradical is *at least* 24 times faster than that of the solvated biradical. This decay ratio matches well with the large lifetime ratio for solvated:unsolvated biradical. Therefore, it is tempting to speculate that the lifetime for this particular biradical may be influenced by the rates of its chemical decay. Unfortunately, this explanation consistent with part of the results is difficult to reconcile with the temperature independence and the effects of paramagnetic additives. The alternative is to repostulate a macroscopic solvent effect on intersystem crossing.[57] We are currently studying other 1,5-biradicals in hopes of obtaining more satisfying explanations. Whatever the eventual outcome, it is clear that our understanding of solvent effects on both biradicals and perhaps even triplets is far from complete.

Experimental Section

***o-tert*-Butylbenzophenone** was prepared following literature procedures.[58] *o*-Bromo-*tert*-butylbenzene was prepared from *tert*-butylbenzene by nitration (para), bromination (ortho), reduction to an aniline, and reduction of the diazonium salt.[59] The Grignard reagent was then prepared and reacted with benzoyl chloride. After routine workup, the product was recrystallized from wet ethanol as white platelets: mp 70–71.6 °C (lit.[58] mp 71–72 °C); IR (CCl_4) 2980, 2860, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 9 H), 7.04 (d, 1 H), 7.20 (t, 1 H), 7.41 (t, 2 H), 7.55 (t, 2 H), 7.84 (d, 2 H), ~7.38 (1 H) (J = 2 Hz for all aromatic protons); ^{13}C NMR δ 32.17, 36.24, 124–148 (12), 200.16; MS *m/e* 238 (18), 223 (4), 208 (39), 195 (28), 161 (100), 160 (50), 105 (56), 77 (74). The *tert*-butyl singlet showed no signs of broadening down to −90 °C in acetone-d_6.

Irradiation Procedures. Steady-state studies were performed in two ways. Samples at MSU were placed in 13 × 100 mm Pyrex tubes, degassed, sealed, and irradiated with the 313-nm region of a 450-W Hanovia mercury arc which was isolated with a K_2CrO_4 filter.[60] A solid sample was prepared by dissolving a few crystals of OTBBP in a few drops of methylene chloride and then allowing the solution to evaporate on a small Pyrex plate. This plate was then placed in a 13 × 100 Pyrex tube which was fitted with a septum and outgassed with nitrogen before being irradiated. All samples being irradiated were held in a room-temperature water bath.

At the NRC samples were placed in cells prepared from 7 × 7 mm square Suprasil tubing, fitted with septa, outgassed with nitrogen, and irradiated in a special housing containing "350"-nm Rayonet lamps. One sample was irradiated for 30 min at ambient temperatures (~30 °C) with 4 lamps while another was placed in a Dewar filled with liquid nitrogen and irradiated for 45 min with 12 lamps. The latter sample was judged to have received 4.5 times as much light. Product appearance was measured by GC–MS. The 30 °C sample had produced 37% indanol, the 77 K sample only 6.5%. Another series of samples, one at room temperature and another in a Dewar cooled to −90 °C, was subjected to 1200 308-nm pulses of an excimer laser. Disappearance of OTBBP was measured by UV. For the low-temperature samples there was a 60% drop in the intensity of the n,π^* band in methanol and a 5% reduction in toluene. The room-temperature toluene sample showed the same amount of ketone disappearance; the methanol sample was complicated by the buildup of a strong absorption between 330 and 400 nm.

Product Identification. HPLC (silica column, 98:2 hexane/ethyl acetate eluent) and GC (5% SE-30 column at 175 °C or capillary bonded phase, programmed temperature) analysis of benzene or methanol solutions of OTBBP irradiated to only a few percent conversion by any of the methods just described revealed one major product and a small, variable (2–10%) amount of another product only during GC analysis. GC–MS analysis revealed that the major product is isomeric with OTBBP while the minor byproduct has lost water. A 50-mL benzene solution containing 100 mg of OTBBP was divided among several Pyrex tubes which were degassed, sealed, and irradiated at 313-nm until no ketone remained. Evaporation of the combined solutions and recrystallization of the residue from hexane provided 3,3-dimethyl-1-phenyl-1-indanol as white platelets: mp 83–84 °C; IR (CCl_4) 3600, 2950, 1440, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 3 H, Me), 1.47 (s, 3 H, Me), 1.95 (br s, 1 H, exchangeable OH), 2.38, 2.44 (AB quartet, 2 H, J = 4 Hz), 7.0–7.6 (m, 9 H, aromatics); MS (*m/e*) 238, 220 (86), 205 (100).

The minor byproduct was not isolated and was identified as 3,3-dimethyl-1-phenyl-1-indene on the basis of its spectra and its likely formation from the indanol: (GC) MS *m/e* 220 (89), 205 (100); ^1H NMR δ 1.39 (s, 6 H) and 6.42 (s, 1 H). That this byproduct is formed by dehydration of the indanol during analysis and workup was indicated by NMR monitoring of the irradiation of OTBBP in methanol-d_4. After some 50% reaction no vinyl signal at δ 6.4 was visible.

Quantitative studies of product formation were performed as usual by parallel irradiaton of degassed samples and of valerophenone actinometers.[47] Product yields in methanol and benzene were measured by GC analysis relative to 0.001 M hexadecane as an internal standard. Solvent effects on product yields were measured by comparing the sum of indene and indanol yields to that of unreacted ketone, as determined by GC analysis. Sensitized naphthalene triplet absorption at 420 nm was measured relative to a γ-methylvalerophenone actinometer which had the same OD at 337 nm as the samples containing OTBBP plus methylnaphthalene.[19] The highest concentration of methylnaphthalene contributed only 10% to the total absorption at 337 nm.

Instrumentation. The flash kinetics apparatus has been described.[61] NMR spectra were recorded at 250 MHz on a Brucker WM-250. GC–MS analysis was performed on a Hewlett-Packard Model 5995 instrument at 70 eV ionizing voltage. GC analysis was performed on Varian Model 1400 machines with FID detectors and recording integrator. Phosphorescence was measured on a Perkin-Elmer Model LS5 spectrofluorimeter with pulsed excitation.

X-ray analyses were performed at room temperature with Picker FACS-I diffractometers. Lattice dimensions were determined with Mo Kα, (λ = 0.709 30 Å) radiation. Intensity data were gathered with Mo Kα radiation ($2\theta_{max}$ = 50°), which at MSU yielded 2483 total unique data and, based on $I > 2\sigma(I)$, 1153 observed data. The data were reduced,[62] structures were solved by direct methods,[63] and refinement was

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by full-matrix least-squares techniques.[64] The final R value was 0.051. The same details for the NRC data are $2\theta_{max} = 45°$ with 1851 unique data which, when treated with profile analysis,[65] yielded 1116 reflections with $I_{net} \geq 2.5\sigma(I_{net})$. The data were processed with the NRC VAX system,[66] and the final R value was 0.036. The final Fourier map showed densities ranging from +0.35 to −0.35 with no indication of missing or incorrectly placed atoms. Computer-generated figures were drawn on an Apple computer by typing the X-ray coordinates into the program "Molecular Animator".[67]

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Registry No. 2, 97337-16-1; OTBBP, 22679-53-4; 3,3-dimethyl-1-phenyl-1-indanol, 24387-75-5.

Supplementary Material Available: Five tables of positional parameters, bond lengths, bond angles, and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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Possible Biomimetic Synthesis of β-Lactams

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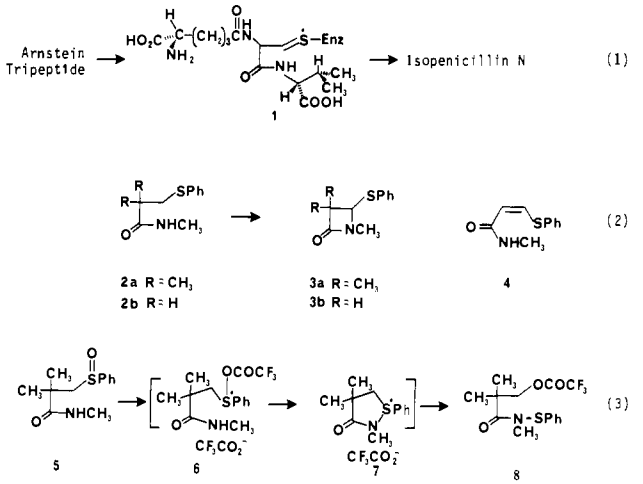
Abstract: The first successful syntheses of β-lactams via a Pummerer rearrangement of the corresponding sulfoxides are described. Thus, variously substituted 3-(phenylsulfinyl)propionamides were converted to 4-(phenylthio)-2-azetidinones in 14–50% yields with trimethylsilyl trifluoromethanesulfonate and triethylamine. The sulfonium ion intermediate in the Pummerer rearrangement may be considered as a chemical equivalent of the proposed intermediate involved in the biosynthesis of β-lactam antibiotics.

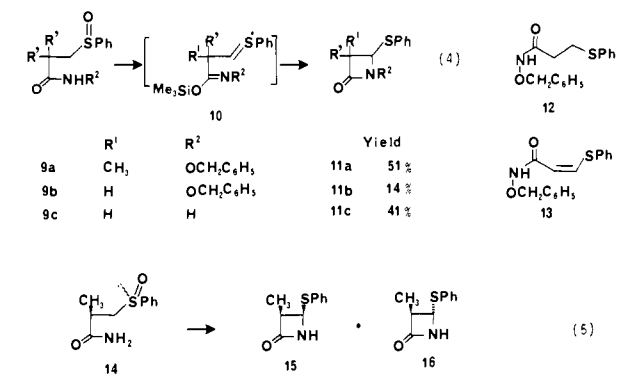
Ever since the structures of penicillins and cephalosporins were elucidated, the biosynthesis of these compounds has been the center of intense research.[1] Although the exact mechanism of conversion of the Arnstein tripeptide, δ-(L-α-aminoadipyl)-L-cysteinyl-D-valine (ACV), to penams and cephems is unknown, Baldwin and co-workers[2] have shown recently that the β-lactam ring is formed first during the enzymatic conversion of ACV into isopenicillin N. Many elegant works have been carried out to probe the biosynthesis of β-lactam antibiotics. Presently, there are three general mechanisms which are consistent with the results of these studies.[3] One of them might be represented by eq 1 in Scheme I.

A Pummerer reaction[4] of the appropriate sulfoxide may be considered to generate a chemical equivalent of the enzymatic system such as **1**. In this paper the first β-lactam synthesis via a sulfonium ion similar to **1** is reported. Historically, there are some previous attempts to effect such a transformation. For example, Wolfe and co-workers have reported that cyclization of

Scheme I



Scheme II



	R'	R²	Yield
9a	CH_3	$OCH_2C_6H_5$	11a 51%
9b	H	$OCH_2C_6H_5$	11b 14%
9c	H	H	11c 41%

S-phenylcysteinamide sulfoxides to β-lactams could not be achieved under Pummerer rearrangement conditions.[5] Beckwith

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