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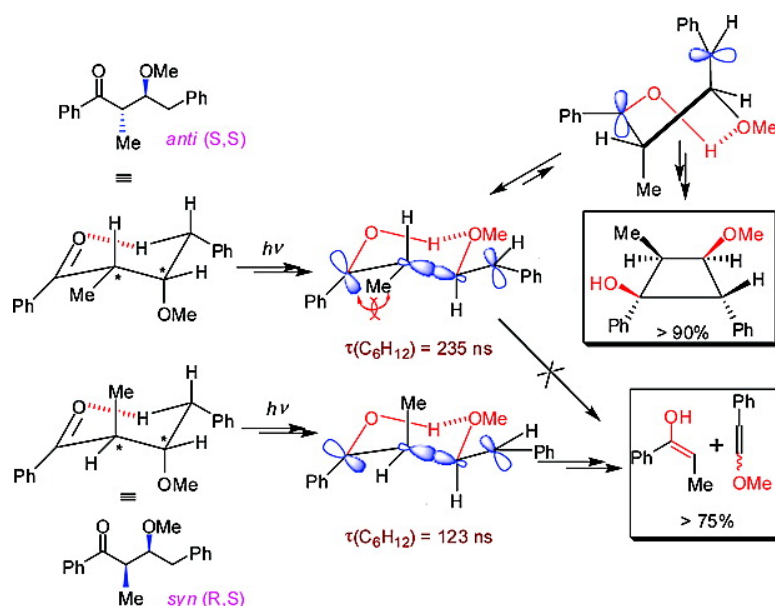
Intramolecular O#H···O Hydrogen-Bond-Mediated Reversal in the Partitioning of Conformationally Restricted Triplet 1,4-Biradicals and Amplification of Diastereodifferentiation in Their Lifetimes

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Intramolecular O−H···O Hydrogen-Bond-Mediated Reversal in the Partitioning of Conformationally Restricted Triplet 1,4-Biradicals and Amplification of Diastereodifferentiation in Their Lifetimes

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Abstract: The photoreactivity and nanosecond transient phenomena have been investigated for a rationally designed set of ketones **4**−**9** in order to gain comprehensive insights concerning the influence of *intramolecular* hydrogen bonding on (i) the lifetimes of triplet 1,4-biradicals and (ii) the partitioning of the latter between cyclization and elimination. Comparisons of the photochemical results and lifetime data for the biradicals of ketones **6** versus **8** and **7** versus **9** revealed a remarkable influence of hydrogen bonding when superimposed upon steric factors: while **6** and **7** yielded cyclobutanols in poor yields, cyclization was found to be overwhelmingly predominant for **8**-*anti* and moderately so for **9**-*anti*, with a high stereoselectivity in the formation of cyclobutanols (>95% for **8**-*anti*). The diastereochemistry in the case of **8** permitted the occurrence of fragmentation or cyclization almost exclusively (>90% cyclization for **8**-*anti* and >75% elimination for **8**-*syn*). Significantly, the intramolecular hydrogen bonding in the biradicals of **8** and **9** was found to reverse their partitioning between cyclization and elimination compared with the behavior of the biradicals of ketones **3**; the ketones **8**-*anti* and **9**-*anti* underwent cyclization in benzene, predominantly leading to cyclobutanols with syn stereochemistry between the C2 and C3 substituents. In accordance with photoproduct profiles, an unprecedented ∼2-fold difference in the lifetimes of the intermediate diastereomeric triplet biradicals of ketones **8** in nonpolar solvents (e.g., $\tau_{syn} = 123$ ns and $\tau_{anti} = 235$ ns in cyclohexane) was observed via nanosecond laser flash photolysis, while no such difference in lifetimes was found for the triplet biradicals of acetoxy ketones **9**. The intriguing diastereodifferentiation in the lifetimes of the diastereomeric triplet 1,4-biradicals of **8** and the product profiles of ketones **6**, **7**, and **9** are best reconciled via a unified mechanistic picture in which superposition of steric factors over varying magnitudes of O−H···O hydrogen bonding selectively facilitates a particular pathway. In particular, the diastereodifferentiation in the photochemical outcomes for the diastereomers of ketone **8** and in the lifetimes of their triplet biradicals can be understood on the basis of rapid deactivation of the **8**-*syn* triplet biradical via fragmentation and slow cyclization of the **8**-*anti* triplet biradical from chair- and twist−boat-like hydrogen-bonded conformations, respectively. The photolysis in polar aprotic solvents such as DMSO and pyridine was found to reverse the chemoselectivity, yielding reactivity paralleling that of ketones **3**, for which the steric factors between the C2 and C3 substituents control the photochemical outcome.

Introduction

One of the fundamental photoreactions of ketones that contain a hydrogen atom at the γ-position is the Norrish type-II reaction.[1] Since its discovery,[2] there has been continual interest in this reaction from the point of view of understanding the photoreactivity of dialkyl and aryl alkyl ketones in general[1] and the behavior of the intermediate triplet 1,4-biradicals in
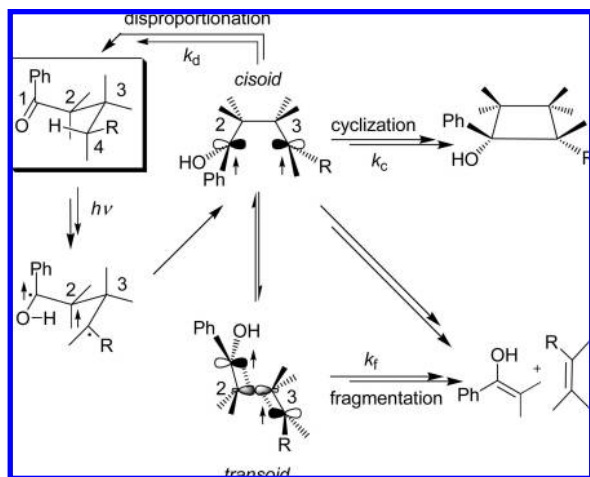
particular;[1,3] the latter are abundantly generated in both thermal and photochemical processes.[4] Mechanistically, initial γ-hydrogen abstraction by the triplet states of ketones via a six-membered cyclic transition state leads to cisoid triplet 1,4-biradicals, which may collapse by three possible pathways,

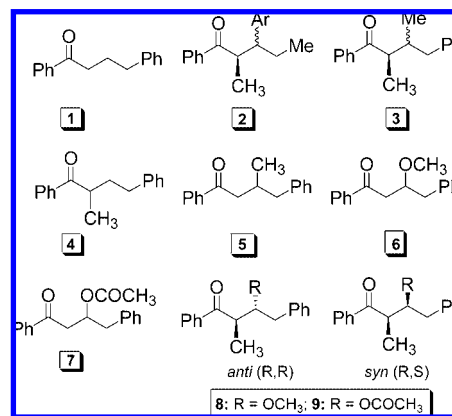† Indian Institute of Technology.
‡ Jacobs University Bremen.

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Scheme 1. Various Pathways for the Collapse of Norrish Type-II Triplet 1,4-Biradicals

disproportionation

k_d

cisoid

cyclization k_c

$h\nu$

k_f fragmentation

transoid

Chart 1

anti (R,R) *syn* (R,S)

8: R = OCH$_3$; **9:** R = OCOCH$_3$

namely, (i) internal disproportionation (with rate constant k_d), (ii) cyclization (k_c), and (iii) fragmentation (k_f), as shown in Scheme 1 for a representative phenyl alkyl ketone.[1] Internal disproportionation of the initial triplet 1,4-biradical subsequent to intersystem crossing results in regeneration of the starting ketone and is generally responsible for the less-than-unity photodecomposition quantum yields usually observed.[1] The cisoid conformation may undergo cyclization when the two singly occupied orbitals are directed toward each other.[1a,5] Although the fragmentation may proceed from both the cisoid and transoid conformations, it is generally ascribed to the latter because cyclization is kinetically favored from the cisoid conformation. There exist two schools of thought concerning the partitioning of triplet 1,4-biradicals between cyclization and fragmentation, namely, spin inversion accompanying product formation[1b,6] and intersystem-crossing geometries controlling 1,4-biradical reactivity.[3c,7] Be this mechanistic dichotomy as it may, at present there appears to be no clear-cut understanding of how the triplet biradicals partition themselves between the cyclization and fragmentation pathways, although their geometries appear to crucially control the product profiles. Insofar as the lifetimes of triplet 1,4-biradicals are concerned, the influence of conformational factors, substituents, solvents, etc.[3d,8−10] continue to be as intriguing as they were two decades ago.[3e,h]

We have recently shown that conformational restrictions imposed via α,β-disubstitution of γ-phenylbutyrophenone **1** offer unique opportunities for investigating the diastereodiffer-

entiating photochemistry of ketones **2** and **3** (Chart 1) and the associated transient phenomena.[9] In the present investigation, we have examined the behavior of O−H···O hydrogen-bonded triplet 1,4-biradicals derived from the rationally designed set of ketones **6**−**9** and contrasted the results with those for simple biradicals derived from ketones **3**−**5** (Chart 1). The 1,4-biradicals of ketones **3**−**9** are bisbenzylic, and the location of substituents at the β-position in **6**−**9** permits intramolecular O−H···O hydrogen bonding via a six- or eight-membered ring.[11−13] Herein, we show that intramolecular hydrogen bonding in diastereomeric triplet 1,4-biradicals of conformationally restricted ketones **8** and **9** in benzene solution diverts the preferred pathways of partitioning based on steric effects. Photolysis in a strongly hydrogen-bond-accepting polar aprotic solvent such as DMSO or pyridine leads to the reversal of the biradical partitioning pathways observed in benzene. Intramolecular hydrogen bonding in cyclohexane amplifies the diastereodifferentiation[14] to such an extent that the diastereomeric 1,4-triplet biradicals of ketone **8** exhibit an unprecedented ~2-fold difference in their lifetimes, as revealed by nanosecond laser flash photolysis.

Results

Synthesis of Ketones 4−9. Ketones **4** and **6**−**9** were prepared starting from the products of Aldol reaction of acetophenone or propiophenone with phenylacetaldehyde, as described in the Supporting Information. The acetophenone Aldol products were converted to **6** and **7** by methylation and acetylation reactions using MeI/Ag$_2$O/diethyl ether[15] and Ac$_2$O/CoCl$_2$/CH$_3$CN[16] or Ac$_2$O/DMAP/DCM conditions, respectively. The diastereomeric

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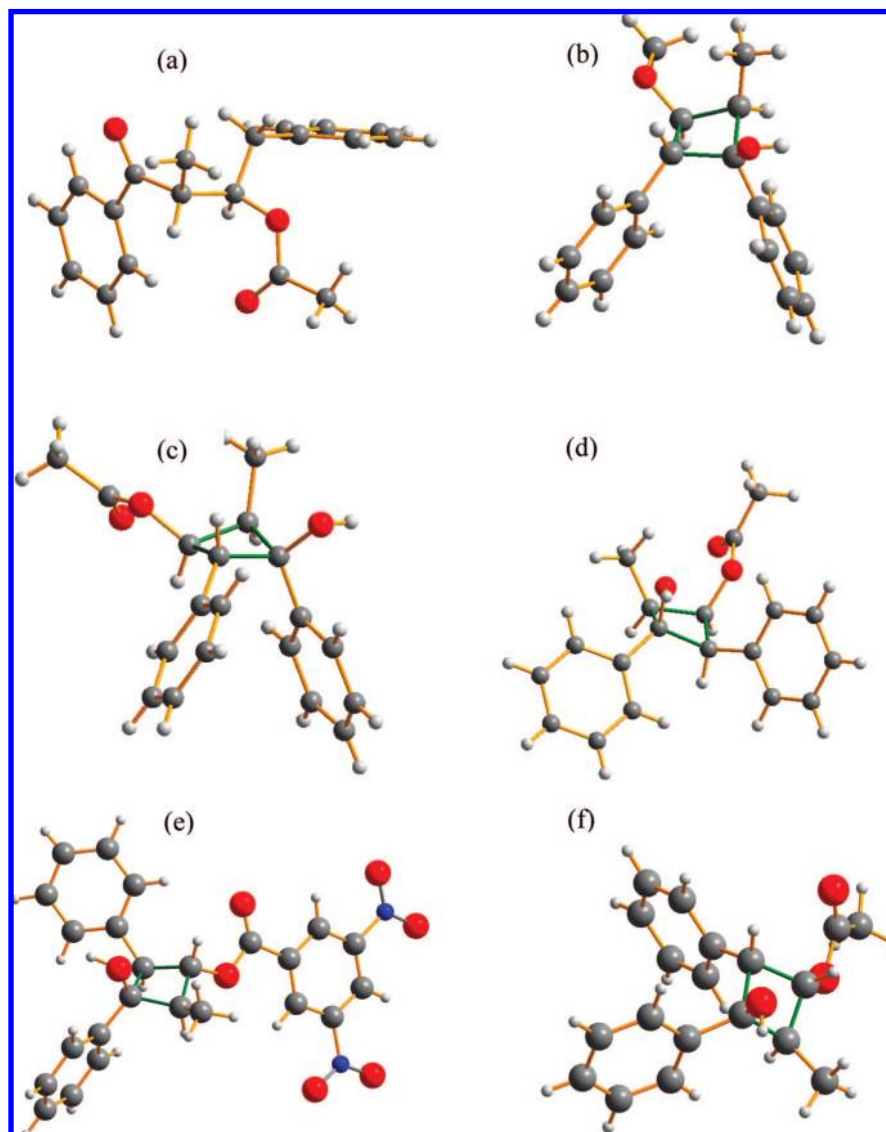
Figure 1. Molecular structures of (a) ketone **9**-*anti* and the cyclobutanols obtained from photolysis of (b) **8**-*anti*, (c, d) **9**-*anti*, and (e, f) **9**-*syn*. It should be noted that cyclobutanol CB1 of **9**-*syn* was hydrolyzed and the resultant dihydroxy product derivatized as a 3,5-dinitrobenzoyl ester. In (b−d), the substituents at carbons C2 and C3 (Me and OMe/OAc, respectively) are syn, while in (e, f), the C2 and C3 substituents (Me and OCOAr/OAc, respectively) are anti.

syn and anti aldols derived from the Aldol reaction of pro-piophenone with phenylacetaldehyde were separated, and each diastereomer was converted to its methoxy (**8**) or acetoxy (**9**) analogue via the same approach as for **6** or **7**, respectively. Ketone **5** was prepared by 1,4-conjugate addition of α,β-unsaturated butyrophenone with PhCH$_2$Cu(CN)ZnBr, as described in the Supporting Information.[17]

The stereochemistries of the methoxy and acetoxy diastereomers were established by X-ray crystal structure determination of one of the diastereomers of acetoxy ketone **9**, which was found to be anti (Figure 1). On this basis, the aldol that led to **9**-*anti* as well as the methoxy ketone **8** derived from this aldol were assigned anti stereochemistry. Of course, the other diastereomer in each case was assigned syn stereochemistry by default.

Photolysis of Ketones 4−9 and Characterization of Photoproducts. The photobehavior of ketones **4−9** was examined by steady-state irradiation of their solutions (contained in pyrex tubes) in a photoreactor fitted with 350 nm lamps. In qualitative

experiments, the progress of reaction and formation of products were monitored by TLC and ^{1}H NMR analyses. For all cases except ketones **6** and **8**-*syn*, the Norrish type-II photoproducts (i.e., cyclobutanols, acetophenone/propiophenone, and olefin) were the sole products; for **6** and **8**-*syn*, tetrahydrofuranol derivatives were found to be formed in ~4 and 15−20% yields, respectively, via competitive δ-hydrogen abstraction (eq 1):[6,12a]
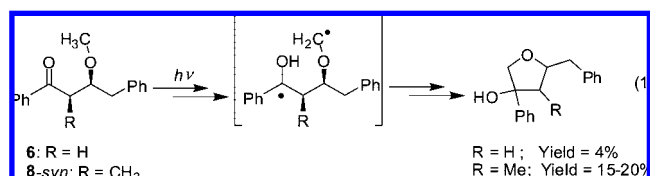
In the case of **8**-*syn*, a small amount (~2−5%) of a new cyclobutanol with stereochemistry similar to that of the cyclobutanol CB1 derived from the anti diastereomer was also found (Table 2).[18]

In preparative-scale photolyses involving ~0.5–1.0 mmol of the ketone, cyclobutanols were isolated in each case. The isolated yields of the cyclobutanols obtained from ketones **4–9** are given in Table 1. The stereochemical assignments of the structures of the cyclobutanols obtained from diastereomeric ketones **8** and **9** were made on the basis of X-ray crystal structure determinations and nuclear Overhauser effects (NOEs) in ^{1}H NMR spectroscopy (see the Supporting Information). More specifically, the structures of the cyclobutanols derived from **8**-*anti* and **9**-*anti* were determined by X-ray crystallography. The stereochemistries of the cyclobutanols derived from **8**-*syn* were established on the basis of NOE effects and the chemical shifts of the methyl groups; the methyl group that has a hydroxy group on the adjacent carbon of the cyclobutanol in a syn relationship generally exhibits downfield shift by ~0.3 ppm.[12b,19] As the major cyclobutanol product of **9**-*syn* was not crystalline, it was hydrolyzed under MeOH/K$_2$CO$_3$ conditions to the corresponding diol, and the latter was esterified with 3,5-dinitrobenzoyl chloride to yield a crystalline derivative suitable for X-ray diffraction studies (eq 2).
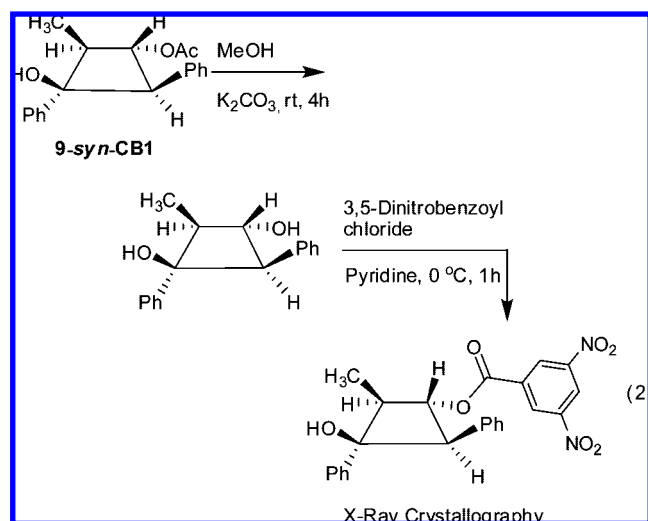
However, the minor cyclobutanol product was a solid that crystallized readily in a mixture of ethyl acetate and petroleum ether. In the case of **8** and **9**, it should be noted that for the cyclobutanols derived from the anti and syn diastereomers of the ketones, the X-ray structures as well as the NOE experiments revealed that the stereochemical relationships between the substituents at C2 and C3 are syn and anti, respectively (Figure 1); this is very pertinent for providing mechanistic insights into the behavior of the precursor triplet biradicals, as discussed below.

A perusal of the results from photolysis in benzene collected in Table 1 shows that α-methyl substitution increased the yield of cyclobutanols while β-methyl substitution decreased it. The β-methoxy and β-acetoxy substituents in **6** and **7**, respectively, modified the yield of cyclobutanols by 6–14% relative to that observed for the methyl analogue **5**. Cyclization yields and the stereochemistries and relative ratios of the cyclobutanols derived from **8** and **9** are given in Table 2, along with the corresponding

Table 1. Yields of Cyclobutanols Formed upon Photolysis of Ketones **1–9** in Benzene and Lifetimes of Their Respective Triplet 1,4-Biradicals in Various Solvents

		product yields (%)[a]		triplet biradical lifetimes (ns)[b]			
entry	ketone	cyclization	fragmentation	benzene	DMSO	cyclohexane	MeOH
1	**1**[c]	10	90	–	–	55[c]	146
2	**3**-*anti*[d]	<7	>93	71	–	61	161
3	**3**-*syn*[d]	66	34	65	–	46	158
4	**4**	43	57	90	162	70	160
5	**5**	26	74	50	136	35	135
6	**6**	20 (4)[e]	80	94	87	100	90
7	**7**	34	66	84	105	78	105
8	**8**-*anti*	>90	<10	232	95	235	145
9	**8**-*syn*	<10 (15)[e]	>75	141	90	123	110
10	**9**-*anti*	51	49	110	102	95	120
11	**9**-*syn*	54	46	99	114	85	115

[a] The photolyses (λ = 350 nm) were carried out on solutions in dry benzene under a N$_2$ gas atmosphere for 8–10 h. The reported values refer to isolated yields, with the remainder identified as elimination products by ^{1}H NMR spectroscopy (see the Supporting Information). [b] Determined by fitting the decay of the transient absorptions at 310 nm to a single exponential function, with errors of ±10%; typically, 8–15 × 10^{-3} M solutions of the ketones (OD@355 nm ≈ 0.15) were subjected to laser flash photolysis. [c] For product distributions and lifetimes in heptane, see refs 5b and 3d, respectively. [d] Data taken from ref 9b. [e] The value in parentheses is the isolated yield of the tetrahydrofuranol derivative formed by initial δ-hydrogen abstraction.

results from photolysis of the α,β-dimethyl-substituted analogue **3**. Particularly noteworthy are the large yields of cyclobutanols from the **8**-*anti* (>90%) and **9**-*anti* (51%) diastereomers (Table 1, entries 8 and 10), for which the cyclization should be disfavored on the basis of simple steric considerations, as in the case of the α,β-dimethyl-substituted analogue **3**-*anti* (see below). Furthermore, one observes that the cyclobutanols were formed with high stereoselectivity from **8**-*anti* and predominantly from **9**-*anti* (Table 2, entries 2 and 5).

The dependence of the product distributions on the solvent was investigated in more detail for ketones **8** and **9** using the polar aprotic solvents DMSO and pyridine, which act as strong hydrogen-bond acceptors of the intermediary triplet 1-hydroxy-1,4-diphenyl-1,4-biradicals.[8b,20] For the anti diastereomers of **8** and **9**, photolysis in DMSO and pyridine led to cyclobutanols in considerably lower yields (Table 2). For **8**-*anti*, the yield of cyclobutanol dropped from >90% in benzene to ~25% in DMSO and pyridine, suggesting that the elimination is promoted. In contrast, cyclization was found to be enhanced for **8**-*syn*: the yield of cyclobutanols was found to increase from 10% in benzene to ~50% in DMSO and pyridine. Notably, a mixture of two cyclobutanols together with 15–20% tetrahydrofuranol derived from initial δ-hydrogen abstraction[6,12a] was obtained (entries 9–11, Table 2). A similar albeit less pronounced trend with variation of the solvent from benzene to DMSO/pyridine was observed for the photolysis of **9**. The structures of all of the cyclobutanols were established by X-ray crystallography and/or NOE experiments.

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Table 2. Results of Preparative Photolysis of Ketones **8** and **9** in Different Solvents[a] Compared with Those of Ketones **3**[b] in Benzene

				ratio of cyclobutanols[d]	
entry	ketone	solvent	cyclization yield (%)[c]	CB1	CB2

1	**3**-*anti*	benzene	<6-7	—[e]	—[e]
2	**8**-*anti*	benzene	>90	>98	—[f]
3		pyridine	27	>98	—[f]
4		dimethyl sulfoxide	22	>98	—[f]
5	**9**-*anti*	benzene	51	66	34
6		pyridine	24	100	—[f]
7		dimethyl sulfoxide	30	100	—[f]

8	**3**-*syn*	benzene	<66	>97	—[e]
9	**8**-*syn*	benzene	<10(15)[g]	50	—[h]
10		pyridine	47(20)[g]	82	12[h]
11		dimethyl sulfoxide	54(16)[g]	85	12[h]
12	**9**-*syn*	benzene	54	90	10
13		pyridine	68	92	8
14		dimethyl sulfoxide	68	94	6

[a] All of the photolyses were conducted under a N_2 atmosphere in a photoreactor fitted with 350 nm lamps. Mass balances for all cases were >90% as monitored by ^{1}H NMR spectroscopy. [b] Data from ref 9b. [c] Isolated yield. [d] Normalized to 100%. [e] Not characterized. [f] Not detected. [g] Isolated yield of the tetrahydrofuranol derivative formed by initial δ-hydrogen abstraction (see text). [h] The remainder was another cyclobutanol with stereochemistry similar to that of CB1 derived from **8**-*anti* (see text).

Nanosecond Laser Flash Photolysis and Lifetimes of the Transient Triplet 1,4-Biradicals. The transient phenomena for ketones **4**−**9** were studied by subjecting their solutions to laser flash photolysis at 355 nm. The concentrations of the solutions were ~8−15 × 10^{-3} M with an optical density (OD) of ~0.15. Laser flash photolysis produced a strong transient absorption for all of the ketones **4**−**9** at ~310−320 nm and a weak, broad band at 400−450 nm in cyclohexane and 400−550 nm in benzene.[21] These absorption spectra are characteristic of hydroxyphenylmethyl and benzylic radicals.[9b,22,23] The typical absorption spectra recorded for the two representative diastereomers of ketone **8** in cyclohexane and benzene are shown in Figure 2.

On the basis of a comparison of the absorption features with those reported for **1** and closely related analogous ketones,[9,23] the transients of ketones **4**−**9** were assigned to the bisbenzylic triplet 1,4-biradicals generated by Norrish type-II hydrogen abstraction from the γ-benzylic site; the ketones undergo γ-hydrogen abstraction to afford triplet biradicals quantitatively.[24] The assignment of the transients to triplet 1,4-biradicals was independently verified by quenching studies involving piperylene. It has been reported by Caldwell et al.[3d] that the transient absorption in the unsubstituted ketone **1** and its closely related analogues was not affected by a diene such as isoprene up to concentrations as high as 0.1 M. In our experiments, the lifetimes of the transients of the representative cases **8**-*syn* and **8**-*anti* were found to be similarly unaffected by 1,3-pentadiene at a concentration of 0.06 M, but the absorbances of the transients decreased. This suggests that the added quencher

intercepts the precursors of the triplet biradical intermediates. From changes in the initial absorbances of the transients and the assumption of diffusion-controlled quenching by 1,3-pentadiene, lifetimes of the triplets of the diastereomeric ketones **8** were estimated to be ~10 ns as an upper limit.

The decay kinetics for ketones **4**−**9** were determined at 310 nm. The transient decays were found to be monoexponential, and the fits afforded the triplet biradical lifetimes (each the mean of three or more independent experiments) reported in Table 1. As can be seen, the lifetimes in most cases were relatively longer in the polar protic methanol solvent than in cyclohexane or benzene;[8b] in view of the short triplet lifetimes, photolysis in solvents such as cyclohexane and methanol are less likely to lead to products of reactions with solvent. Otherwise, a more discernible and meaningful trend is noteworthy in cyclohexane and benzene solvents: α-methyl substitution in **4** increased the lifetime relative to **1** while β-methyl substitution in **5** had the opposite effect (Table 1, entries 1, 4 and 5). The methoxy and acetoxy substituents at the β-position increased the lifetimes, with a more pronounced effect being observed for the former (entries 6 and 7). While only a marginal difference was observed for the two diastereomers of acetoxy ketone **9** (entries 10 and 11), a remarkable discrimination was found for the syn and anti diastereomers of α-methyl-β-methoxy ketone **8** (entries 8 and 9): the triplet biradical lifetime of the anti diastereomer was found to be ~2-fold higher than that of the syn diastereomer in the nonpolar solvents.

Discussion

Alkyl phenyl ketones react predominantly from their triplet states, and those that contain a γ-hydrogen react to yield triplet 1,4-biradicals quantitatively.[24] As mentioned earlier, the less-than-unity quantum yield generally observed for ketone disappearance is traceable to internal disproportionation of (hydrogen back-transfer in) the triplet 1,4-biradicals (Scheme 1).[1] It has long been known that α- and β-substituents influence the partitioning of triplet 1,4-biradicals between cyclization and elimination. The strong dependence of the photochemical outcome on the location of the substituent(s) has been reconciled on the basis of the influences of stereochemical and electronic factors on the geometries of the transition states for cyclization and elimination; the transition state favoring cyclization requires overlap of the radical orbitals, while that for elimination must

(21) The transient absorption spectroscopy of more dilute solutions of ketones **6**, **8**, and **9** using 308 nm excimer lasers was complicated by the observation of an intriguing transient absorption with a maximum at ~390 nm. This unexpected absorption, which seemingly submerged the shoulder in the 400−450 nm region, was found to be significantly stronger for the anti diastereomer than for the syn counterpart. Furthermore, the species responsible for the transient absorption was found to be long-lived (τ ≈ 1.5−2.0 μs). From control experiments with partially and fully photolyzed samples, it was firmly established that the transient absorption originated from the photoproducts of certain ketones that were formed and excited instantaneously during the laser flashes. As the additional transient did not interfere during experiments using 355 nm irradiation (the third-harmonic of a Nd−YAG laser), where the aryl ketones fortunately displayed a sufficiently strong absorption (ε ≈ 35 M^{-1} cm^{-1}), the spectral acquisitions and lifetime determinations were carried out at this wavelength. Further studies are in progress to characterize and unravel the origin of these unexpected transients, which were also noted for the first time in our previous study (ref 9a). The results of these investigations will be reported in due course.

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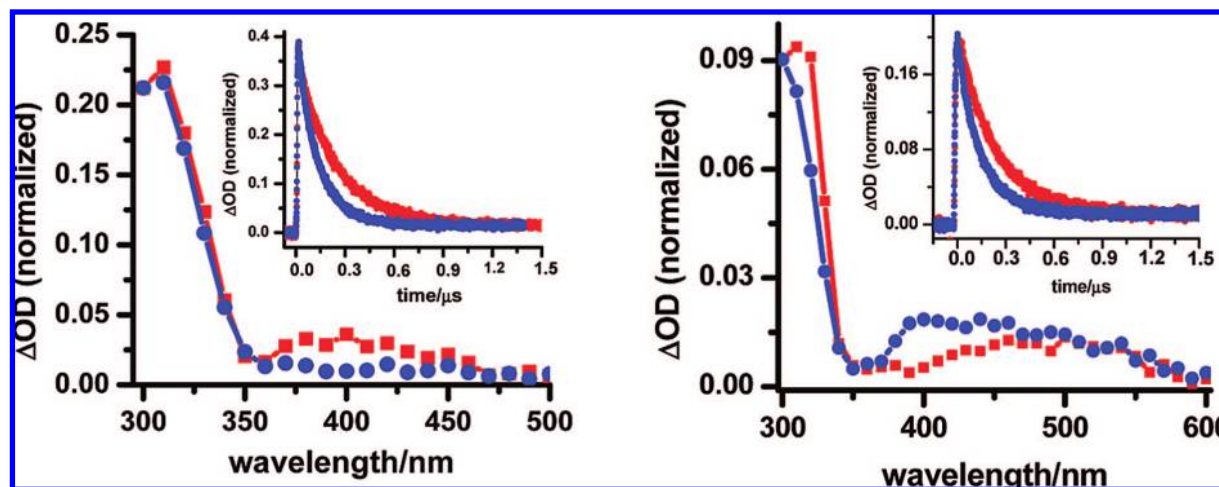
Figure 2. Transient absorption spectra of triplet 1,4-biradicals generated by 355 nm nanosecond laser flash photolysis of (red squares) **8**-*anti* and (blue circles) **8**-*syn* in (left) cyclohexane (recorded 70 and 50 ns, respectively, after the laser pulse) and (right) benzene (recorded 110 and 70 ns, respectively, after the pulse). The insets show the decay profiles for (red) anti and (blue) syn diastereomeric triplet 1,4-biradicals of ketones **8** in the corresponding solvents.

Scheme 2. Mechanistic Rationalization of the Formation of Predominant Products from the syn and anti Diastereomers of Ketones **3**
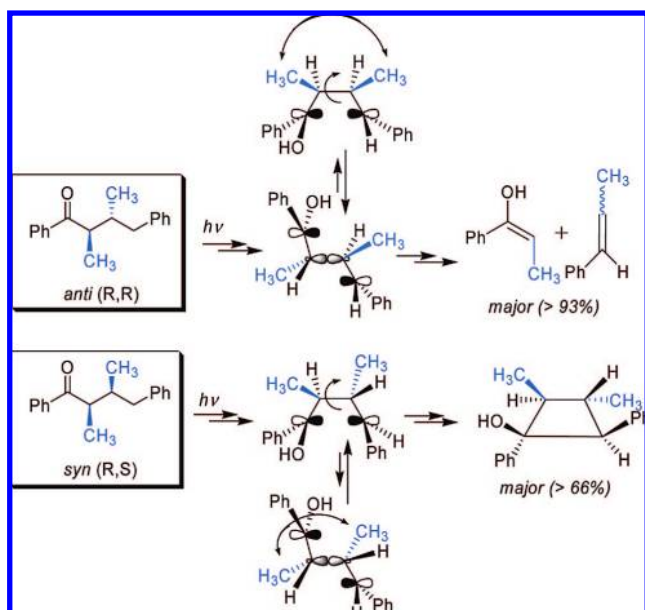
entail maximum overlap of the p orbitals of the two radical centers with the C2−C3 σ bonding orbital.[1,5] It must also be mentioned that the stereochemical requirements are thought to be more stringent for elimination than for cyclization.

We have recently shown that the diastereodifferentiating photobehavior of α,β-disubstituted ketones can be reconciled on the basis of (i) stereocontrolled stabilization of the geometry (cisoid/transoid) of the derived triplet biradical and (ii) the premise that cyclization will be observed only if the triplet biradical assumes the cisoid geometry while fragmentation occurs predominantly from the transoid geometry.[9b] As shown in Scheme 2, the divergent product profiles from the syn (66% cyclization) and anti (>93% elimination) diastereomers of ketone **3** are understood in terms of the biradical conformations

(24) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480.

that are favored on the basis of steric considerations alone: steric repulsion between the methyl groups at C2 and C3 in the cisoid conformation of the biradical of the anti diastereomer favors adoption of the transoid geometry, so elimination is predominantly observed; the opposite holds true for the biradical of the syn diastereomer, for which cyclization becomes the major pathway. Clearly, the stereochemical considerations simplify rationalizations based on spin-statistical factors,[3c] spin−orbit coupling efficiencies and associated geometries,[7] etc. Of course, implicit in our criteria of favored conformations for partitioning of the intermediate triplet 1,4-biradicals is the fact that the latter are sufficiently long-lived for equilibrium to be established between the various conformations. This is likely to be true when the triplet biradical lifetimes are on the order of tens of nanoseconds, which is the case, in particular, for bisbenzylic biradicals such as those generated from the ketones investigated herein.

We adhere to the same mechanistic formulation to understand the photochemistry of ketones **4−9**. As the intermediate triplet 1,4-biradicals are uniformly bisbenzylic for all of the ketones, the differences in the photochemical outcomes for **4−9** (i.e., cyclization vs elimination) as well as the lifetimes of the triplet 1,4-biradicals in Table 1 should again be explicable by the differences in the conformational preferences of the biradicals that arise from the varying substitution patterns at either the α or β positions (**4−7**) or both (**8** and **9**).

Effect of α- and β-Substituents on and Intramolecular O−H⋯O Hydrogen-Bond-Mediated Reversal of 1,4-Triplet Biradical Partitioning. The effect of simple alkyl substitution at the α and/or β positions will be considered first. The parent unsubstituted γ-phenylbutyrophenone **1** affords cyclization products only in 10% yield (Table 1).[5b] While the β-methyl group in **5** exerts only a small effect on the product distribution (entry 5), α-methyl substitution in **4** raises the cyclization yield quite steeply to 43% (entry 4).[5a] This can be traced to the fact that the biradicals of ketones containing an α-substituent would be subject to severe 1,2-eclipsing interactions between the α-substituent and the hydroxyl/phenyl group, preventing the p orbitals of the radicals from aligning parallel with the C2−C3 σ bond in the transoid conformation.[5] For the biradicals of ketones **6−9**, intramolecular hydrogen bonding additionally

Scheme 3. Mechanistic Rationalization of the Formation of Photoproducts of Diastereomeric Ketones
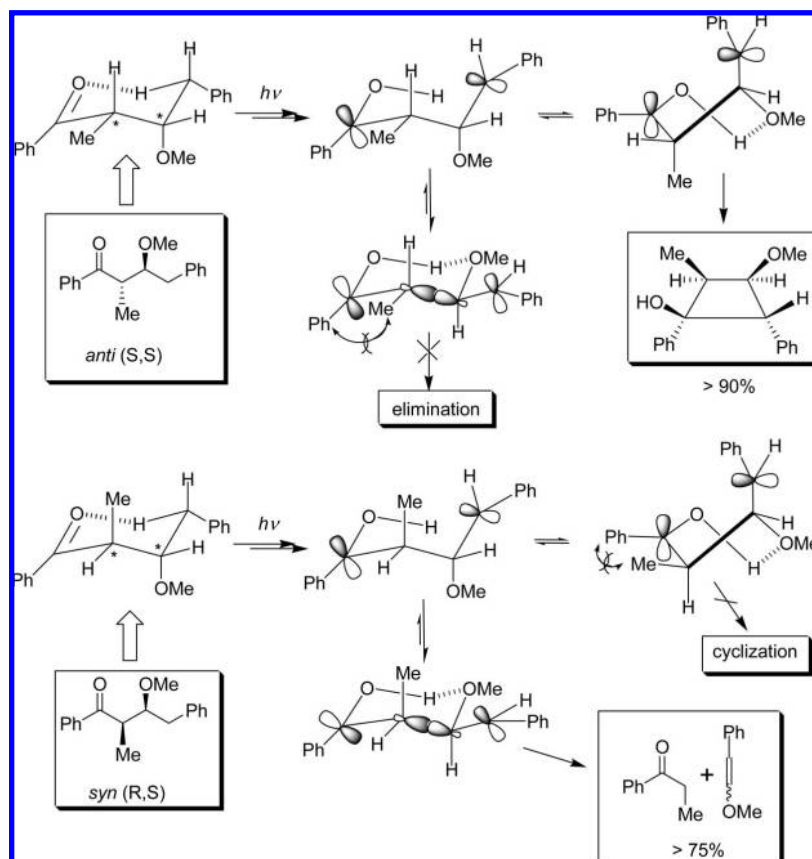
interferes, modifying the conformational preferences and hence the product distributions. We shall first discuss the diastereo-differentiating reactivity of ketones **8** and **9** and then consider a rationalization of the photobehavior of ketones **6** and **7**.

For ketones that are α,β-disubstituted, the steric interactions between the C2 and C3 substituents in the biradicals of the syn and anti diastereomers determine the conformational preferences and the partitioning between cyclization and elimination. As described earlier, the triplet biradical of ketone **3**-*syn* preferentially adopts the cisoid conformation, leading to predominant cyclization (Scheme 2), and the cyclobutanols are formed with anti stereochemistry between the C2 and C3 substituents. In contrast, the transoid conformation is favored for the biradical of the **3**-*anti* diastereomer, so elimination is the major pathway. Indeed, the photobehavior of α-acetamido ketones observed by Griesbeck et al.[7c,11a] can also be nicely accommodated within this mechanistic paradigm of stereocontrolled stabilization of cisoid/transoid conformation and associated reactivity. However, this trend was found to be reversed for photolysis of ketones **8** and **9** in benzene in that the anti diastereomers predominantly afford cyclization products, leading to cyclobutanols with syn stereochemistry between the substituents at C2 and C3, while the syn diastereomers predominantly undergo elimination (Table 2); the syn stereochemistry of the cyclobutanols in the former case was unequivocally established by X-ray crystal structure determinations (Figure 1). Furthermore, a very high diastereo-selectivity is observed for the formation of cyclobutanol from **8**-*anti*. Clearly, the arguments based on steric effects alone are inadequate in these cases, and the dramatic reversal in the product profiles for **8** and **9** compared with those for **3** should be attributed to intramolecular hydrogen-bonding effects.

Scheme 3 shows the consequences of photoexcitation of the syn and anti diastereomers of α-methyl-β-methoxy ketone **8**. γ-Hydrogen abstraction by triplet excited ketones via six-membered cyclic transition states yields the corresponding triplet 1,4-biradicals, which may directly undergo intramolecular hydrogen bonding in a nonpolar solvent such as benzene. Indeed, the location of the methoxy group in both diastereomers of **8** permits O−H···O hydrogen bonding of the triplet 1,4-biradical in a chair geometry. For the biradical of the anti diastereomer, the singly occupied p orbitals lie apart in the hydrogen-bonded chair conformation, precluding cyclization. Also, the elimination does not appear to be facile because of the fact that the p orbital of the hydroxyphenyl radical cannot align parallel with the C2−C3 σ bond; analysis of a ball-and-stick model revealed that the location of the methyl group in the equatorial position hinders such an arrangement. Nevertheless, the hydrogen-bonded chair conformer of the 1,4-biradical of the anti diastereomer is likely to undergo elimination, since cyclization cannot occur because the radical centers in this conformation lie so far apart. On the other hand, a simultaneous rotation about the C2 and C3 carbons in opposite directions may lead to a hydrogen-bonded twist−boat geometry in which the radical p orbitals may be oriented nicely for cyclization to become a predominant pathway. In fact, the stereorelationship between the substituents in the twist−boat is exactly transferred to the cyclobutanol, whose structure was established by X-ray crystallography (Figure 1). For the syn diastereomer, the hydrogen-bonded triplet biradical would be devoid of the steric inhibition of collinearity of the p orbitals with the C2−C3 σ bonding orbital that occurs in the case of the anti diastereomer; the methyl group at C2 would occupy the axial position, readily promoting elimination.

The reactivity from the higher-energy twist−boat conformation may not arise at all in this case.

Poor selectivity in the partitioning between cyclization and elimination in the biradicals of the acetoxy derivatives **9**, which is reflected in the cyclization and elimination yields (Table 1), can similarly be reconciled on the basis of hydrogen-bonding and stereoelectronic factors. As the hydrogen bonding in these cases would occur via an eight-membered ring, the biradical geometries should be less rigidly defined. Thus, the stereoelectronic arguments discussed above for the biradicals of ketones **8** should also be less stringent, accounting for the lower cyclization yield as well as the poorer diastereoselectivity in the formation of cyclobutanols for the anti diastereomer in benzene. A comparison of the photochemical results for ketones **8** and **9** with those for **6** and **7** is compelling from a mechanistic point of view. The poor cyclization yields in the latter two ketones due to the absence of an α-methyl substituent underscore the importance of conformational restrictions on the triplet 1,4-biradicals that undergo intramolecular hydrogen bonding. The low cyclization yields should be explicable in terms of competitive elimination from the hydrogen-bonded chair conformer (Scheme 3).

Solvent Effects. The photobehavior of the diastereomeric ketones **8** and **9** in the nonpolar benzene solvent illustrates the effect of intramolecular hydrogen bonding on the otherwise conformationally restricted (by α,β-disubstitution) triplet 1,4-biradicals, which may partition between two distinct pathways. As intramolecular hydrogen bonding is prone to be destroyed intermolecularly by strongly hydrogen-bond-accepting solvents, ketones **8** and **9** represent unique cases for deconvoluting the hydrogen-bonding and steric effects and exploring the extent to which solvents can modify the partitioning of the derived triplet 1,4-biradicals. As one may envisage, the exclusion of intramolecular hydrogen bonding should cause the steric interactions between the C2 and C3 substituents to become decisive in determining the conformational preferences and hence the photochemical outcomes in a manner akin to that observed for the biradicals of ketones **3**. We have photolyzed **8** and **9** in two polar aprotic solvents, DMSO and pyridine, which solvate triplet hydroxyl-1,4-biradicals and enhance quantum yields of decomposition by suppressing internal disproportionation back to the precursor ketones (Scheme 1).[20] The results in Table 2 show that the cyclization yield for **8**-*anti* dropped from >90% in benzene to ∼25% in the polar aprotic solvents, while that for **8**-*syn* increased from <10% to ∼50%. Alternatively, elimination and cyclization became predominant for the anti and syn diastereomers, respectively, of ketone **8** in the polar aprotic solvents. This is in accordance with the trend observed for ketones **3**, whose triplet biradicals undergo partitioning solely based on steric factors.

Amplification of Diastereodifferentiation in the Triplet Lifetimes of the Bisbenzylic 1,4-Biradicals. As the triplet biradicals of ketones **4**−**9** are uniformly bisbenzylic, they readily lend themselves to detection by nanosecond laser flash photolysis. For all of the ketones, the lifetimes of the triplet biradicals followed a regular trend in the two nonpolar solvents cyclohexane and benzene (Table 1). The data for ketones **1**, **4**, and **5** suggest that α- and β-methyl groups exert opposing effects on the biradical lifetimes: while the α-Me group increased the lifetime, the β-Me group decreased it slightly. Incidentally, the hydrogen-bonding substituents (OMe and OAc) increased the lifetimes despite being located at the β-position. For the diastereomeric biradicals of ketones **8**, we observed an ∼2-fold

difference in the lifetimes in cyclohexane and benzene, which attests to H-bond control of the deactivation. This differentiation in the lifetimes of the syn and anti diastereomers (123 and 235 ns, respectively, in cyclohexane) is remarkably higher than what we previously documented for ketones **3** for the first time.[9b]

In principle, the lifetimes of triplet 1,4-biradicals are determined by internal disproportionation (k_d), cyclization (k_c), and fragmentation (k_f) (Scheme 1). While different rates of internal disproportionation might apply for the triplet biradicals of **1**−**8**, we found that their partitioning between the other pathways (i.e., cyclization and elimination) as reflected in the product analyses can be nicely correlated with their triplet biradical lifetimes. Accordingly, α-substituents that hinder elimination appear to increase the lifetimes (Table 1, entry 4), as do β-substituents that stabilize the biradicals via intramolecular hydrogen bonding (entries 6 and 7). The β-methyl substituent that seemingly offers less hindrance to elimination reduces the lifetime (entry 5). In other words, any factor that affects elimination appears to influence the lifetimes in a more pronounced way. Thus, the diastereomeric differentiation observed in the lifetimes of the biradicals of ketones **8** can be reconciled on the basis of retardation of elimination (or lack thereof) in their hydrogen-bonded chair conformations. Incidentally, it is the location of the α-methyl group that controls elimination. As may be seen from Scheme 3, the methyl group hinders elimination in the case of the anti biradical but exerts no such influence on the syn biradical. Rather less perceptible differentiation in the lifetimes of the diastereomeric biradicals of **9** should be attributed to weaker hydrogen bonding (if any exists) via an eight-membered ring, which augments the stereoelectronic requirement for elimination.

In contrast to the lifetimes of the triplet biradicals in benzene, those in MeOH and DMSO do not fit into a readily conceivable pattern. Nonetheless, the lifetimes observed for the biradicals of diastereomeric ketones **8** in DMSO are quite instructive. As this solvent may exclude the influence of intramolecular hydrogen bonding, the lifetimes should be expected to be controlled largely by steric factors; of course, the latter modify the conformational preferences and partitioning pathways. A perusal of the lifetimes in Table 1 reveals almost similar lifetimes for the diastereomeric biradicals of ketones **8** and **9** (Table 1, entries 8−11), pointing to the absence of intramolecular hydrogen-bonded stabilization of the biradicals. The product distributions discussed above for the diastereomers of **8** and **9** in DMSO and benzene nicely correlate with the lifetime data. It thus emerges that the conformational factors, at least in polar solvents, are less likely to drastically affect the lifetimes of triplet 1,4-biradicals, insofar as they are subject to mere steric factors. However, the lifetimes in conjunction with the product profiles observed here for the diastereomeric biradicals of ketones **8** in nonpolar solvents confirm the dramatic influence of intramolecular hydrogen bonding and disprove the conclusion reached by Caldwell and co-workers[3e,h] nearly two decades ago, namely, that the lifetimes of triplet biradicals are invariant to conformational factors.

Generalizations Regarding the Chemoselectivity (Cyclization versus Fragmentation) of Hydrogen-Bonded Triplet 1,4-Biradicals. The triplet hydroxy-1,4-diyls generated via photoinduced γ-hydrogen abstraction may in principle be intramolecularly hydrogen-bonded in a number of cyclic geometries, depending on the location (i.e., α, β, γ, or δ) as well as the nature of the heteroatom-containing groups. Thus, the manner in which the intramolecular hydrogen-bond-controlled geometries of the triplet

Scheme 4. Ketones Whose Triplet Biradicals May Be Intramolecularly Hydrogen-Bonded via Five- to Eight-Membered Cyclic Geometries and their Yields (%) of Photoinduced Yang Cyclization
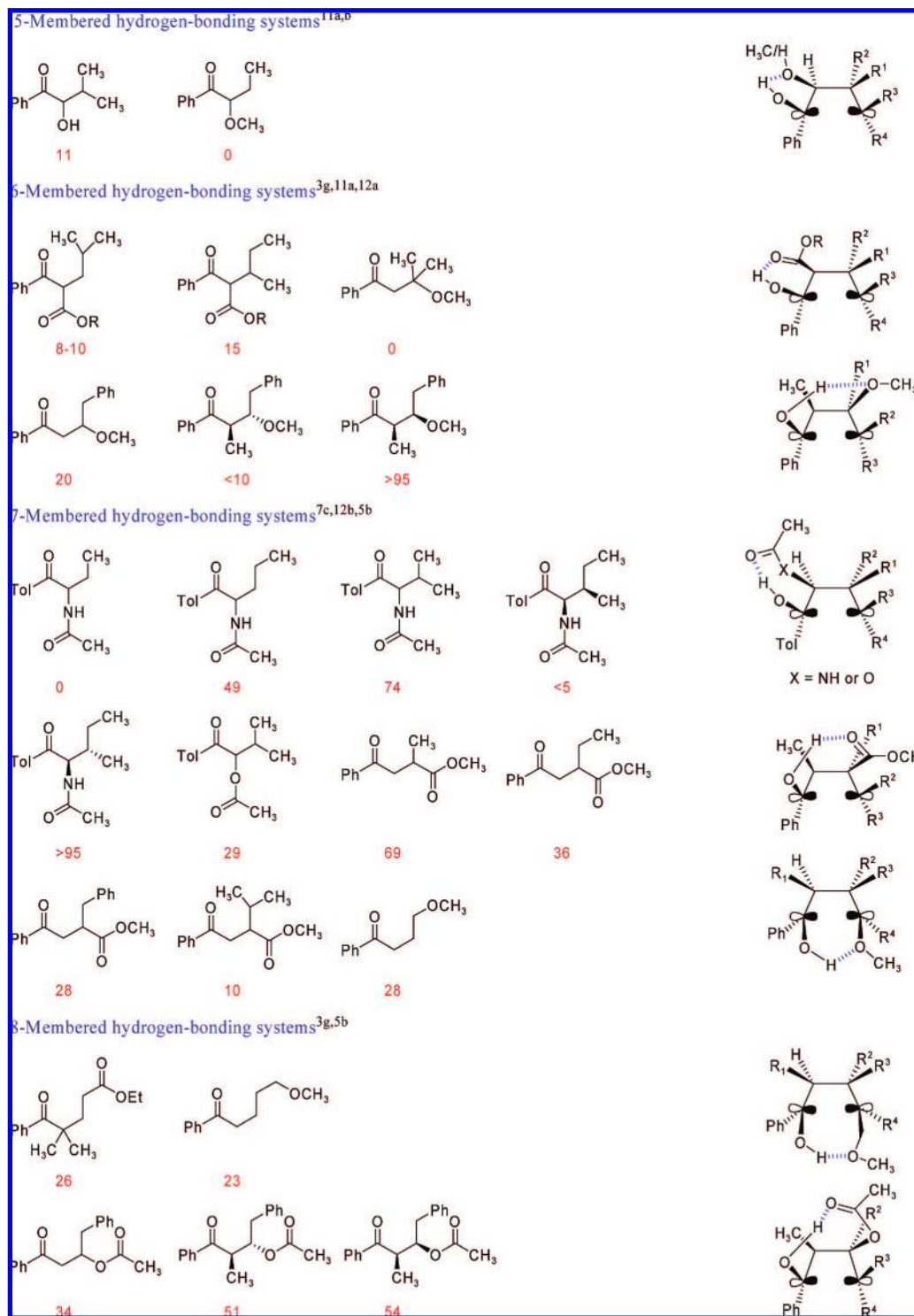
biradicals affect their partitioning between fragmentation and cyclization as well as the stereochemistry of the product cyclobutanols is of fundamental importance. Scheme 4 categorizes a variety of ketones whose triplet biradicals may be internally hydrogen-bonded via five-, six-, seven-, or eight-membered cyclic geometries. Also given for each case is the yield of cyclization product(s). A perusal of the latter data shows that hydrogen-bonding-controlled geometries influence cyclization yields significantly. For example, the yields of cyclobutanols from methoxy-substituted butyrophenones vary from 0 to 28%

for α-, β-, and γ-methoxybutyrophenones. Remarkably, the steric congestion in hydrogen-bonded biradicals results in enhancement of cyclization yields, as observed for a range of α-acetamido ketones[7c] with increasing methyl substitution (see the seven-membered hydrogen-bonding systems in Scheme 4). However, the fact that the chemoselectivity (i.e., cyclization vs fragmentation) depends crucially on the stereodisposition of the substituents emerges from the diastereodifferentiating photobehavior observed for both the α-acetamido ketones and β-methoxybutyrophenones of the present study; the triplets of

the former and the latter may hydrogen bond via seven- and six-membered rings, respectively. Although it is evident from Scheme 4 that the chemoselectivity varies with the strength of intramolecular hydrogen bonding as well as the triplet biradical geometry, it is the superposition of steric and hydrogen-bonding interactions (as in the methoxy ketones **8**) that appears to permit one of the two disparate pathways (either cyclization or fragmentation) to be observed almost exclusively. While steric effects alone may bring about high chemoselectivity, as we have shown previously for **3**,[9b] the present study illustrates that intramolecular hydrogen bonding in conjunction with steric interactions reverses the chemoselectivity based on steric effects alone. Further, it also emerges from a comparison of the photochemical results for ketones **8** with those for the acetoxy analogues **9** that the almost exclusive occurrence of either fragmentation or cyclization depends crucially on steric as well as rigid hydrogen-bonded geometries, as in the case of **8**; indeed, weaker hydrogen bonding in triplet biradicals has been shown by Griesbeck et al.[7c,11a] to affect both cyclization efficiency and diastereoselectivity.

Conclusions

Comparisons of the photochemical results and lifetime data for the biradicals of ketones **6** versus **8** and **7** versus **9** have revealed a remarkable influence of hydrogen bonding superimposed upon steric factors: while **6** and **7** yielded cyclobutanols in poor yields, cyclization became overwhelmingly predominant for **8**-anti and moderately so for **9**-anti, with a high diastereoselectivity in the formation of cyclobutanols (>95% for **8**-anti). The diastereochemistry in the case of **8** permitted the occurrence of either fragmentation and cyclization almost exclusively (>90% cyclization for anti and >75% elimination for syn). Most significant is the fact that the intramolecular hydrogen bonding in the biradicals of **8** and **9** reversed their partitioning between cyclization and elimination compared with the behavior of the biradicals of ketones **3**: the ketones **8**-anti and **9**-anti predominantly underwent cyclization in benzene, leading to cyclobutanols with syn stereochemistry between the C2 and C3 substituents. Photolyses of **8** and **9** in hydrogen-bond-accepting solvents such as DMSO and pyridine yielded dramatically modified product distributions that reflected photochemistry paralleling that of ketones **3**, for which the intermediate biradicals cannot undergo intramolecular hydrogen bonding. The nanosecond laser flash photolysis studies revealed an unprecedented diastereodifferentiation in the lifetimes of the triplet 1,4-biradicals of ketones **8** in nonpolar solvents: the syn and anti triplet biradicals exhibited an ∼2-fold difference in their lifetimes. The intriguing product stereochemistry and the accompanying dramatic variation in the lifetimes of the diastereomeric triplet 1,4-biradicals of **8** as well as the product

profiles of ketones **6**, **7**, and **9** can be best reconciled via a unified mechanistic picture in which superposition of varying magnitudes of O−H···O hydrogen bonding over steric factors selectively facilitates a particular pathway. In particular, the diastereodifferentiation between the photochemical outcomes for the diastereomers of ketone **8** and the lifetimes of their triplet biradicals are readily rationalized by rapid deactivation (**8**-syn) and slow cyclization (**8**-anti) from chair- and twist−boat-like hydrogen-bonded conformations of the corresponding triplet biradicals, respectively.

The behavior of 1,4-biradicals in general continues to be an enigma. Attempts to understand the factors that influence the lifetimes of triplet 1,4-biradicals and their modes of partitioning continue to be of contemporary interest in view of the importance of the Norrish type-II reaction in several applications.[22,25] In particular, Yang cyclization and Norrish fragmentation are being increasingly explored in asymmetric synthesis,[14b,26] photocyclizations,[27] photorelease of volatiles,[28] and photodeprotections[29] and as probes of microenvironments.[30] Since 1,4-biradicals are also intermediates in Paterno−Buchi cycloaddition reactions,[7a,b] we believe that the insights uncovered in this work significantly enhance our understanding of the behavior of triplet 1,4-biradicals as important reactive intermediates.

Supporting Information Available: Experimental details of synthesis and photolysis of ketones, characterization details of photoproducts (including figures showing the NOE interactions), description of laser-flash-photolysis studies, transient absorption spectra of valerophenone in cyclohexane and benzene, and details of the X-ray crystal structure determination and CIF files for all of the crystal structures in Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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