of **1**, diverting the course of the reaction toward formation of **3**.[18] It is clear that one function of the Lewis acid is to react with **5**, thus preventing the decarbonylation of **1** by **5**. However, this does not appear to be its only task. An understanding of the detailed role(s) of the Lewis acid is being sought.

The importance of formylmetal complexes as intermediates in homogeneous Fischer–Tropsch processes has recently been underscored.[4,5,19] *N*-Acylimidazole–transition-metal reactions provide a potential route to a variety of acyl transition-metal complexes, including formylmetal derivatives. We are currently examining the synthetic scope and mechanistic aspects of the transition-metal–*N*-acylimidazole reactions.

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Registry No. 1, 3197-61-3; **2**, 14878-31-0; **3**, 80327-81-7; **4**, 53558-55-7; **5**, 5587-42-8; **7**, 2466-76-4; **8**, 64867-63-6; BF_3, 7637-07-2; triethylboron, 97-94-9; trimethoxyboron, 121-43-7.

Supplementary Material Available: A table of ^1H and ^{13}C chemical shift data for imidazole, *N*-formylimidazole, and sodium imidazolate in the presence and absence of Lewis acids (1 page). Ordering information is given on any current masthead page.

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[18] While Et_3B and BF_3 were less effective in this regard, they appeared to form stronger complexes with imidazole and **1** than did $(MeO)_3B$. The complexes were detectible by shifts in the ^1H and ^{13}C resonance positions. No analogous shifts were observed in the $(MeO)_3B$ case.

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Some Structural Effects on Triplet Biradical Lifetimes. Norrish II and Paterno–Buchi Biradicals

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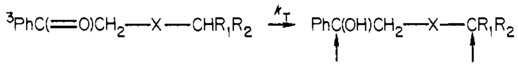
Norrish II biradicals provide remarkably good model systems for the study of triplet biradical properties in general, especially in cases for which the triplet ketone precursor is quite short lived.[1] Scaiano[1] has shown that the lifetime generally observed in hydrogen-bonding solvents for valerophenone-derived biradicals is about 100 ns and is largely independent of alkyl substitution at the terminus; typical lifetimes in hydrocarbon solvents are 35–40 ns. We now report that the effect of γ-aryl substituents is to increase the lifetime modestly and that the effect of replacing β-CH_2- by β-O- is to shorten the lifetime dramatically. The latter substitution affords a lifetime similar to that for Paterno–Buchi (preoxetane) biradicals.

The well-known mechanism[1,2] for the Norrish II process is given in eq 1–3. We prepared benzhydryl phenacyl ether expecting that it would afford a Norrish II biradical with convenient spectroscopic properties. The conventional photochemistry is unexceptional. The principal products are benzophenone and acetophenone (initially of course via the enol) in quantum yields of 0.70 ± 0.05 and 0.76 ± 0.06, respectively; the same values are obtained in both methanol and benzene. A secondary product, 1,2-dibenzoylethane, is absent at 8% conversion but is found in 46% yield at completion. Its formation is readily rationalized by excitation of the product Ph_2CO and eq 4–6.

$$PhC({=}O)CH_2{-}X{-}CHR_1R_2 \xrightarrow{h\nu} \xrightarrow{isc} {}^3PhC({=}O)CH_2{-}X{-}CHR_1R_2 \quad (1)$$



$${}^3PhC({=}O)CH_2{-}X{-}CHR_1R_2 \xrightarrow{k_T} Ph\underset{\uparrow}{C}(OH)CH_2{-}X{-}\underset{\uparrow}{C}R_1R_2 \quad (2)$$

1a–g

$$1 \xrightarrow{\tau_{BR}^{-1}} PhC(OH){=}CH_2 + R_1R_2C{=}X \quad (3)$$

(+ cyclobutanols, starting material)

$$^3Ph_2CO + PhC({=}O)CH_2OCHPh_2 \rightarrow Ph_2\dot{C}OH + PhC({=}O)CH_2O\dot{C}Ph_2 \quad (4)$$

$$PhC({=}O)CH_2O\dot{C}Ph_2 \rightarrow Ph_2CO + PhC({=}O)CH_2 \quad (5)$$

$$2PhC({=}O)CH_2\cdot \rightarrow PhC({=}O)CH_2CH_2C({=}O)Ph \quad (6)$$

Quenching by isoprene afforded $k_Q\tau$ for the triplet ketone of 0.63 M^{-1} in benzene and 0.62 M^{-1} in methanol, leading to triplet lifetime estimates of approximately 120–130 ps. There is ample precedent[3] for very rapid γ-hydrogen abstraction in other phenacyl ethers, and the presence of two γ-Ph groups should further increase the rate.[2] The very short triplet lifetime and the expectation that the well-known and easily detected benzophenone ketyl radical[4] would be a good model for the absorption spectrum of the biradical prompted a study of the transient spectroscopy in the system.

We were initially chagrined to find that, utilizing nitrogen laser excitation (3371 Å, ca. 5 mJ, 8-ns fwhm), the only detectable transient was benzophenone triplet, λ_{max} 525 nm,[4] $\tau \sim 300$ ns in CH_3OH,[5] $\phi \sim 0.03$, which we expect is largely or exclusively the result of a biphotonic process. However, using a mode-locked Nd:YAG laser pulse extended to ca. 100 ps (fourth harmonic, 2662 Å, ca. 0.5–10 mJ) and a Tektronix 7912 transient digitizer, we have detected transient absorption in the UV region ($\lambda > 3000$ Å) with lifetime of the order of a few nanoseconds. The fwhm of the combined excitation/response function for the system is ca. 1.75 ns; a (highly reproducible) ringing of modest but nonnegligible intensity requires deconvolution for any transient with $\tau \lesssim 10$ ns.

Table I lists lifetimes and λ_{max} values in the UV region for the Norrish II biradicals. Our lifetime for the valerophenone derived biradical **1f** is in excellent agreement with the literature value;[1] λ_{max} in the UV region has not been previously reported. Its extinction coefficient is at least tenfold larger than that at its λ_{max} in the visible region.[6]

The transient **1a** from benzhydryl phenacyl ether is clearly not the corresponding triplet, especially since it is unaffected by 0.5 M isoprene and since the triplet lifetime from steady-state quenching is so short. It can only be assigned as the biradical **1a**. The observed spectrum is consistent in that the rather broad shape may reflect overlapping absorptions of the termini, **1f** being a model for one and benzophenone ketyl[4] (λ_{max} 330 nm) being a model for the other. The lifetime is remarkably short when compared to previously reported valerophenone-derived biradicals;[1] **1b**, with one phenyl replaced by H, is even more short lived. Lifetimes for **1a** and **1b** were obtained as deconvolution fits to the equation $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ by using the scattered laser light detected by the same system as the combined excitation/response function. The two exponential fit assumed a τ_1 of 10 μs, and was required by an observed small increase in base-line absorption (presumably due to absorbing products or unknown biphotonic transients). The ratio A_1/A_2 was always <0.1 and decreased with decreasing laser power.

The biradicals **1c** and **1d** prove that the short lifetime for **1a** is not related to the phenyl groups. Note the monotonic increase in lifetime in both protic and nonprotic solvent in the order of

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[1] Scaiano, J. C.; Lissi, E. A.; Encina, M. V. *Rev. Chem. Intermed.* **1978**, *2*, 139–196 and references therein.

[2] Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168–177 and references therein.

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[4] Bensasson, R. V.; Gramain, J.-C. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1801–1810.

[5] The decay produced the spectrum of benzophenone ketyl, λ_{max} 550 nm, as expected.

[6] For γ-methylvalerophenone, λ_{max} = 415 nm and ϵ_{max} 800 M^{-1} cm^{-1}: Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431–434.

0002-7863/82/1504-0629$01.25/0

Table I

biradical	X	R_1	R_2	MeOH τ,[a] ns	MeOH λ_{max}, nm	heptane τ,[a] ns	heptane λ_{max}, nm
1a	O	Ph	Ph	4.9 ± 1.5[b]	320–330 (br)	6.4 ± 1.6[b]	330
1b	O	Ph	H	1.3	305	1.7	~300
1c	CH_2	Ph	Ph	222 ± 18[c]	330	113 ± 13	330
1d	CH_2	Ph	H	146 ± 18[c]	310	55 ± 8	315
1e	CHPh	Ph	H	95			
1f	CH_2	CH_3	H	93[d]	~320	38[e]	
1g	CH_2	OCH_3	H	70 ± 5	~310	30 ± 6[f]	

[a] Confidence limits where given are twice the standard deviation of repetitive samples from the mean. [b] In the presence of 0.05–0.5 M isoprene; lifetime independent of isoprene concentration. [c] Unaffected (±10%) by the presence of 0.1 M isoprene. [d] This work. [e] Small, R. D.; Scaiano, J. C. *Chem. Phys. Lett.* 1977, *59*, 431–434. [f] A substantial fluorescence, probably derived from a trace impurity, is difficult to time resolve in heptane and renders this value less certain than the rest.

increasing number of phenyl groups: **1f** < **1d** < **1c**. Phenyl groups may increase the lifetime by conjugation with the odd electron at the terminus. Increased delocalization should increase the average distance between the unpaired electrons, thus decreasing spin–orbit coupling.[7] The comparison of **1a** and **1b** follows similarly. The β-phenyl in **1e**[8] appears to shorten its lifetime in comparison to **1d**. We hypothesize that conformational factors are involved. We would expect a larger proportion of the conformation with gauche termini, which brings the termini closer than when trans and thus could increase spin–orbit coupling.[7]

If the short lifetimes for **1a** and **1b** are not due to the phenyl groups, the explanation must derive from the presence of the oxygen in the chain. That the effect is very largely specific to the β position is shown by the lifetime of **1g**. The latter, derived from γ-methoxybutyrophenone,[2] has already been reported to have a $k_Q\tau$ value similar to that of **1f** from thiol trapping experiments.[11] The present results show a lifetime for **1g** only some 25% shorter than for **1f**. The lifetime of **1h** ($X = CH_2$, $R_1 = Ph$, $R_2 = OH$) of 84 ns in methanol[9] represents another example of oxygen at a terminus but not between the termini, and again the effect is small.

A probable contributor to the lifetime-shortening effect of β-O- is the decreased average distance between the unpaired electrons due to the resonance form shown below. Other more speculative explanations might derive from conformations which provide an angle of approximately 90° between the oxygen 2p orbital and the half-filled p orbital at the adjacent terminus. Such conformations will provide maximal spin–orbit coupling.[7] However, since **1g** presumably could also access analogous conformations, we think at present that the latter explanation is unlikely.

The biradicals **1a** and **1b** are in fact the Paterno–Buchi (preoxetane) biradicals which would formally result from addition of benzophenone and benzaldehyde, respectively, to acetophenone enol. We have studied the transient spectroscopy of benzophenone in the presence of tetramethylethylene and ethyl vinyl ether and observe strong signals in the UV region (λ_{max} 330 nm), with lifetimes roughly 1.5–4 ns depending on olefin and conditions. We assign these as the corresponding Paterno–Buchi biradicals[12] and are gratified at the similarity of lifetime and λ_{max} with expectation, on the basis of **1a** and **1b**. Finally, we note that Peters[13] has recently obtained nearly identical results for another Paterno–Buchi biradical. The combination of all these results renders a recent[14] assignment of a 6–25-μs transient on irradiation of benzophenone and 3-methyl-2-pentene as the corresponding Paterno–Buchi biradical unlikely.

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Registry No. **1a**, 80326-01-8; **1b**, 80326-02-9; **1c**, 80326-03-0; **1d**, 80326-04-1; **1e**, 80326-05-2; **1f**, 73461-73-1; **1g**, 34903-03-2.

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(11) Wagner, P. J.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 287–289.

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Application of the Energy Gap Law to the Decay of Charge-Transfer Excited States

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We recently reported the preparation of a series of osmium(II) polypyridyl compounds.[1] The compounds were remarkable because of the suggestion that the properties of their metal-to-ligand charge-transfer [MLCT; $Os^{II} \rightarrow \pi^*$(bpy) or (phen)] excited states including luminescence lifetimes, emission maxima, and redox potentials are systematically variable by making chemical changes. We have now prepared a more extensive series of compounds and with the extended series are able to identify systematic variations in both nonradiative (k_{nr}) and radiative rate constants (k_r), and the systematic variations have important implications for transition-metal photochemistry.

Table I gives some relevant excited-state parameters for a series of mono- and bis-2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) complexes of Os(II). The complexes were prepared by synthetic routes similar to those reported earlier.[1] They were characterized by UV–visible spectra, cyclic voltammetry, and elemental analyses.[2] Emission maxima reported in Table I are corrected for detector sensitivity.[3a] Integrated emission quantum

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