Table I. Excitation Yields of Carbonyl Products from Peroxyls

reaction[a]	solvent, T, °C	[BHN],[b] M	$k_{et}\tau/10^3$	Φ_{ST}[c]	S_T[d]
$2Me_2CHOO^{\bullet} \rightarrow Me_2CO$	Ph-*t*-Bu, 27	0.016	4.1	0.10	3×10^{-5} (5×10^{-6}–5.5×10^{-4})[e]
	MeCN, 28	0.002	1.6	0.05	$(5 \pm 1) \times 10^{-4}$
$2EtOO^{\bullet} \rightarrow MeCHO$	Ph-*t*-Bu, 26	0.0015	1.2	0.20	$(2 \pm 1) \times 10^{-5}$
	MeCN, 31	0.0013	1.6	0.05	$(6 \pm 1) \times 10^{-4}$[f]
$2PhMeCHOO^{\bullet} \rightarrow PhCOMe$	PhEt, 27.6	0.01	0.45	0.07[g]	$(5 \pm 2) \times 10^{-4}$
$2PhCH_2OO^{\bullet} \rightarrow PhCHO$	MeCN, 26	0.0013–0.016	4.6	0.025	$(1 \pm 0.3) \times 10^{-4}$
$2TOO^{\bullet} \rightarrow$ 1-tetralone	Ph-*t*-Bu, 27	0.015	0.60	0.008	$(1 \pm 0.1) \times 10^{-4}$

[a] Reaction sequence 1–3 assumed. [b] Rates of decomposition of BHN in *t*-BuPh calculated from activation parameters in ref 12; in MeCN, we measured $k_d = 1.06 \times 10^{-6}$ s^{-1} at 25.5 °C and assumed $E_a = 27$ kcal/mol to calculate k_d at other temperatures. Cage effects from ref 12 or assumed 10%. [c] Fraction triplet carbonyl that gives excited singlet tDBA in the indicated solvent. [d] Fraction of reaction 3 giving triplet carbonyl products, relative to 3,3,4,4-tetramethyldioxetane (TMD) in the same solvent with $S_T = 0.3$ (ref 10). Average of two or more determinations. Values of k_d for TMD in *t*-BuPh calculated from activation parameters in ref 8. For acetonitrile k_d estimated as 8×10^{-7} s^{-1} at 24.7 °C (extrapolated value in CCl_4 from the following: Kopecky, K. R., et al. *Can. J. Chem.* **1975**, *53*, 1103). [e] Aliquot of TMD added to reaction mixture and S_T calculated from increases in luminescence. [f] Determined relative to S_T for $2Me_2CHOO^{\bullet}$. [g] Determined in *t*-BuPh at 44 °C.

We infer that triplets are the predominant excited state in all cases from reaction 3.[7]

Values of S_T, the fractional excited-state yield of triplets, in Table I are low, from 2×10^{-5} to 6×10^{-4}. The effect of alkyl structure is minor. Differences between S_T for a given peroxyl in the two solvents *t*-BuPh and acetonitrile are at most 1 order of magnitude and comparable to errors in extrapolating the various rate constants. In some cases (e.g., 2-PrOOH in *t*-BuPh), the reproducibility of the experiments was not good.

With the specific values of Φ_{TS} determined here, we can now refine some previously reported values of S_T for the related *alkoxyl* self-reactions:[8]

$$2R_1R_2CHO^{\bullet} \rightarrow R_1R_2CHOH + R_1R_2C{=}O(S_0,T_1) \quad (6)$$

The corrected yields of triplets based on *reacting*, caged alkoxyl pairs derived from hyponitrites[9] are as follows: for acetophenone, 1.5%; for acetaldehyde, 0.12%; for acetone, 1.8%; and for 1-tetralone, 8.3%. These values are quite high and comparable to triplet yields reported from thermolysis of many dioxetanes.[10]

We reported previously[8] that reaction 6 gave the lowest yields of excited states in *t*-BuPh when the carbonyl product was formaldehyde, benzaldehyde, or benzophenone. The triplet energies of these three compounds are 72 kcal or less.[11] Since a higher triplet state of DBA, located at 74.6 kcal, mediates the overall TS energy transfer,[5] eq 4a, it is not surprising that Φ_{TS} would be low for the two aldehydes and negligibly small in the case of benzophenone. In addition, *t*-BuPh was found to quench triplet benzaldehyde, whereas acetonitrile, used here, does not.

From the corrected data corresponding to eq 6 and the data in Table I, we calculate carbonyl product excitation ratios for reaction 6/reaction 3 of 30 for R_1R_2 = 1-phenylethyl, 830 for 1-tetralyl, and about 600 for 2-propyl substituents. For the first two examples, these ratios are larger than those we reported, obtained by an indirect method.[12]

In some cases we have observed that competing luminescent reactions are present in our systems, and it may be prudent to regard our S_T values as upper limits for excitation according to reaction 3. For instance, a value of S_T for the sequence 1–3 could not be carried out with 1-tetralyl hydroperoxide in acetonitrile because, even in the absence of initiator, a relatively high luminescence was observed in this solvent that increased rapidly with time. Similarly, initiated solutions of 2-propyl hydroperoxide in *t*-BuPh containing small amounts of tDBA showed a linear, 5-fold increase in luminescence during 24-h observation. These observations afford potentially valuable insights into slow initiation processes and are under further study.

In summary, values of $S_{triplet}$ decrease in the order of precursor dioxetane > alkoxyl pair ≫ peroxyl pair. The differences in chemiluminescence emission intensities from reactions 6 and 3 with different alkyl groups are due in part to different photophysical pathways for decay of the first-formed triplets, which are generated with efficiencies spanning about a factor of 10 for reaction 3 and a factor of 10^2 for reaction 6. Solvent effects on triplet yields from peroxyl reaction 3 are small from the limited data in Table I. Correspondingly, for self-reaction of 2-propoxyl to give excited acetone in three solvents, the triplet yields differ only by a factor of about 20.[8]

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(7) For six other aliphatic ROOH (*t*-BuPh, 43 °C), we have measured values of $k_{et}\tau$ between 130 and 650.[1] These data are not included in Table I because we have not measured the values of Φ_{TS} for the carbonyl products.

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(9) In nonviscous solvents, reaction 6 is a minor pathway and most of the alkoxyls undergo diffusive escape from the solvent cage.

(10) Adam, W.; Beinhauer, A.; Hauer, H. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, Chapter 12.

(11) (a) Benzophenone, E_T = 69 kcal;[11b] benzaldehyde E_T = 72 kcal;[11c] formaldehyde E_T = 72 kcal.[11d] (b) Carmichael, I.; Hug, G. L. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. I, Chapter 16. (c) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; Table 1-1. (d) Herzberg, G. *Electronic Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, NJ, 1966; p 518.

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Directed Formation of Carbon–Bromine and Carbon–Sulfur Bonds by Tandem Radical Chain Reactions

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We have described the remote chlorination of steroids and flexible chain molecules directed by attached template species.[1] In this process a chlorine atom becomes temporarily bound to the iodine of an iodophenyl template[2] or the nitrogen of a pyridine[3,4] or oxygen of a pyridine *N*-oxide,[5] which are attached as esters to a substrate hydroxyl group. The geometry of the template directs hydrogen abstraction by the complexed chlorine atom. In a second step, the resulting substrate radical then reacts with the

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(3) Breslow, R.; Brandl, M.; Hunger, J.; Adams, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 3799–3801.

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(5) Breslow, R.; Adams, A.; Brandl, M.; Guo, T.; Hunger, J. *Lectures Heterocycl. Chem.* **1987**, *9*, 43–50.

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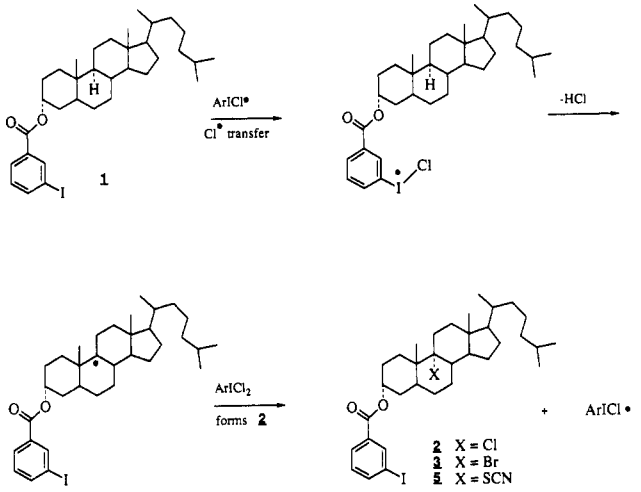
Scheme I

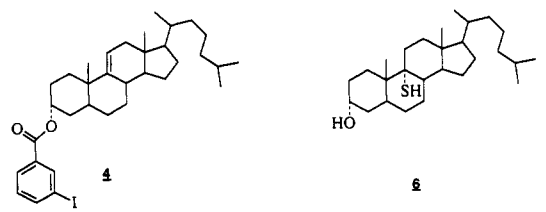


free chlorinating reagent such as $PhICl_2$, SO_2Cl_2, or Cl_2 to form a carbon–chlorine bond and regenerate a species that can transfer Cl• to a new template to continue the chain reaction.

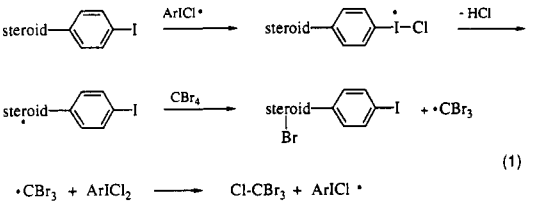
We wanted to generalize this chemistry. In some of the steroid examples[3,6] HCl elimination to generate a desired olefin (such as the 9(11) double bond needed for the synthesis of corticosteroids) is difficult, and Ag^+ was needed to promote it. If instead we had formed a C–Br bond it should eliminate more easily (as we demonstrate below). Furthermore, we wanted to modify our chemistry so as to produce a C–S bond. This could be useful in the synthesis of novel steroid derivatives, such as are used in immunochemistry.

We find that we cannot simply replace the two chlorine atoms in our reagents with bromines or SCN groups, for example. Apparently the Br• and •SCN radicals are too unreactive to be able to abstract hydrogen from unactivated C–H bonds as template complexes. Indeed, only a species as reactive as Cl• seems capable of such H-abstraction after it is stabilized by template complexing. However, we have been able to achieve the desired functionalization chemistry by introducing an additional radical chain reaction that runs in tandem, after the H-abstraction by complexed Cl•. With this scheme we can indeed prepare the desired C–Br and C–S derivatives in good yield, and with our normal geometric control directed by the template.

Photolysis of a 12.5 mM solution of substrate **1** with 1.5 equiv of p-NO_2PhICl_2 in CH_2Cl_2 solution affords the chlorosteroid **2** in >90% yield, as described previously.[1] However, when 20 equiv of CBr_4 is also included, the isolated products are instead the bromosteroid **3** in 32% yield and the 9(11) olefin[1] **4** in 51% yield. The bromosteroid was characterized by ^1H NMR (δ 0.670, 1.137 for C-18 and C-19). On silica chromatography, heating, or even standing it readily eliminated HBr to form the 9(11) olefin **4**. Under these conditions the chlorosteroid **2** is stable, so the bromosteroid is indeed a more useful intermediate for the mild formation of this olefin. The bromosteroid **3** was thus originally formed in 83% yield and partially converted to the olefin product on workup.

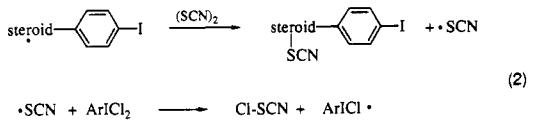


We propose a tandem radical sequence for this conversion (eq 1). No reaction occurs if the $ArICl_2$ is omitted, so we believe that the hydrogen abstraction step is the same as for chlorination. However, the resulting steroid radical can be trapped by the excess of CBr_4, and the CBr_3 radical[7] can then abstract chlorine from $ArICl_2$ to regenerate the ArICl• and continue the chain.



(1)

In another example, we ran the chlorination reaction of 5 mM **1** at 0 °C with $PhICl_2$ and addition of 11 equiv of thiocyanogen[8] ($(SCN)_2$). Now the product was the steroid thiocyanate **5**, isolated by silica chromatography in 64% yield (MS FAB M + 1676, ^1H NMR δ 0.720, 1.143, ^{13}C NMR δ 113.4, and IR 2137 cm^{-1} for SCN). Again no reaction occurred in the absence of the $ArICl_2$, so again we propose a tandem radical process (eq 2). On heating, **5** is converted again to olefin **4** so the SCN group is clearly located on C-9 of the steroid, as our mechanism requires. We have also reduced **5** to the thiol **6** (MS, NMR) with $LiAlH_4$.



(2)

These reactions succeed because higher concentrations of alternative reagents can divert the steroid radical away from chlorination, but the critical template-complexed chlorine atom is still produced after an additional atom transfer process. With the use of such tandem reactions, the scope of template-directed remote functionalization reactions has been considerably broadened.

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Magnetic Properties of *Pseudomonas stutzeri* Nitrous Oxide Reductase

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N_2O reductase is the terminal enzyme in the bacterial denitrification pathway.[5] This enzyme catalyzes the two-electron reduction of N_2O to N_2 in an energy-conserving process.[6] The structural gene (*nosZ*) for *Pseudomonas stutzeri* N_2O reductase has been sequenced[7] and corresponds to a protein of molecular weight 70 kD, whereas the purified enzyme has a molecular weight

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