Highly Efficient Formation of Nitriles and Alkoxy Radicals from *N*-Alkoxybenziminoyl Chlorides in Solution

H. J. Peter de Lijser,* Cassandra R. Burke, Jonathan Rosenberg, and Jordan Hunter

Department of Chemistry and Biochemistry, California State University, Fullerton, California 92834-6866

pdelijser@fullerton.edu

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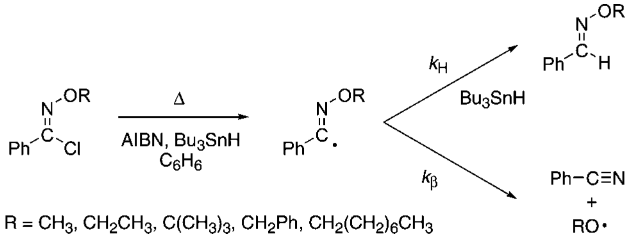

A series of *N*-alkoxybenziminoyl chlorides were synthesized and reacted with tributyltin hydride in the presence of AIBN to generate the corresponding *N*-alkoxybenziminoyl radicals. This methodology successfully generates the desired radicals, which undergo a rapid and highly efficient β-scission reaction, as shown by the formation of the corresponding nitriles and products derived from alkoxy radicals. The intermediate *N*-alkoxybenziminoyl radical could not be trapped by employing high concentrations of Bu_3SnH or by using a hydrogen atom donating solvent such as toluene. The fast β-scission reaction was found to be independent of the structure of the iminoyl chloride. These results are different from studies on the similar *N*-alkyliminoyl radicals, which typically give products from both β-scission hydrogen atom transfer pathways. Using the data from this study as well as some reported rate constants for different hydrogen atom transfer (HAT) processes, we conclude that the lower limit for the rate constant for the β-scission process (k_β) in *N*-alkoxybenziminoyl radicals is 2.5×10^7 s^{-1}.

Introduction

The photooxidation of oximes and oxime ethers derived from ketones typically results in the formation of the parent ketone.[1] Oximes have been proposed to react via iminoxyl radicals, which are formed by deprotonation of the oxime radical cations (Scheme 1).[1] Iminoxyl radicals (**Z**) have also been proposed as intermediates in the generation of NO from arginine, although the involvement of radical ions in that process is not certain.[2]

Further studies involving oxime ethers have shown that these substrates do not form iminoxyl radicals but rather react via deprotonation at the α-position provided a proton is available (Scheme 2).[3] It was found that oxime ethers that lack α-protons are unreactive under those conditions.

Aldoximes react to give both the corresponding aldehyde and the nitrile.[1] The aldehyde is presumably formed via an iminoxyl radical intermediate, however, the pathway and intermediates involved in the formation of the nitrile remain uncertain. We have hypothesized that the formation of nitriles from aldoximes proceeds via *N*-alkoximinoyl radical intermediates.[3,4] This proposal was in part a result of experiments done with *O*-*t*-butylbenzaldehyde oxime, which reacted to give benzonitrile

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* To whom correspondence should be addressed. Phone: (714) 278-3290. Fax: (714) 278-5316.

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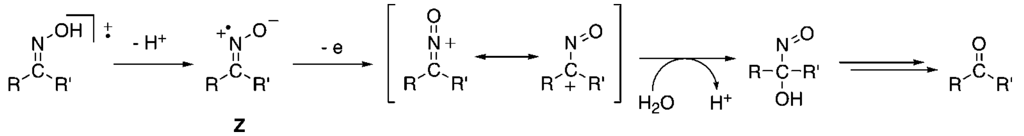
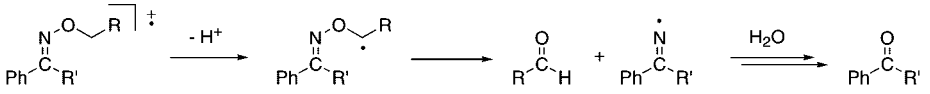
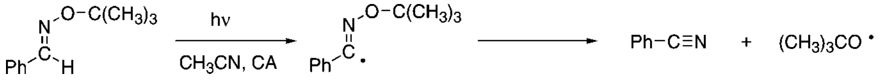
SCHEME 1. Proposed Mechanistic Pathway for the Reactions of Oximes under Photoinduced Electron Transfer Conditions



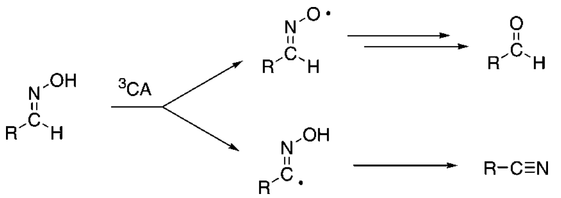
SCHEME 2. Proposed Mechanism for Product Formation in Reactions of Oxime Ether Radical Cations



SCHEME 3. Formation of an *N*-Alkoxybenziminoyl Radical via Hydrogen Atom Abstraction in Oxime Ethers



SCHEME 4. Competitive Hydrogen Atom Abstraction Pathways in Oximes

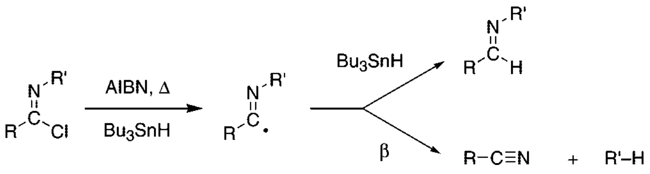


in excellent yield.[5] Since there are no α-hydrogens available in this molecule a reasonable alternative would be hydrogen atom transfer to yield the *O*-*t*-butoximinoyl radical intermediate (Scheme 3).

Similarly, studies on a set of substituted benzaldehyde oximes have suggested that the formation of aldehydes and nitriles in these reactions are best explained by two different pathways that involve different intermediates.[4] When electron transfer is favorable, the preferred pathway involves electron transfer, followed by proton transfer to form an iminoxyl radical, which eventually leads to the formation of the corresponding aldehyde. When electron transfer is unfavorable, a hydrogen atom transfer mechanism will be the dominant pathway. Under the conditions of the reaction, the sensitizer, triplet chloranil (^{3}CA), is expected to be a very good hydrogen atom acceptor. Competition between hydrogen atom abstraction from the hydroxyl group (to form an iminoxyl radical) and from the iminyl carbon (to form an iminoyl radical) would lead to the formation of the aldehyde and nitrile products respectively (Scheme 4).[4]

To learn more about the pathway that leads to the formation of the nitrile products, we decided to focus on the proposed *N*-alkoximinoyl radical intermediates as the potential precursors. These radicals have received very little attention so far. They are similar in structure to *N*-alkyliminoyl radicals, which are better known, especially their use in the synthesis of heterocyclic rings via radical cyclization reactions.[6] Several methods have been developed to generate these types of radicals, including hydrogen abstraction from aldehydes, radical addition to isonitriles, and abstraction of a suitable group such as a halide or a selenide.[6] The most commonly observed reactions of these species are atom abstraction (e.g., hydrogen atom abstraction from tributyltin hydride), β-scission to form a nitrile, α-scission to form an isonitrile, or addition to unsaturated molecules (e.g., alkenes).[6p] Because of their similarities, *N*-alkoximinoyl radicals

SCHEME 5. Formation of *N*-Alkyliminoyl Radicals from Reaction of Iminoyl Chlorides with Tributyltin Radicals



are expected to show much of the same reactivity. There are no reports on the reactivity of *N*-alkoximinoyl radicals nor are there any reported methodologies for generating these reactive intermediates. Wirth and Rüchardt generated *N*-alkyliminoyl radicals from *N*-alkyliminoyl chlorides via chlorine atom abstraction with tributyltin radicals.[6h] The synthesis of *N*-alkoxybenziminoyl chlorides has been reported[7,8] and these chlorides would seem like appropriate precursors for the desired iminoyl radicals. As shown in Scheme 5, the products formed in the reactions *N*-alkyliminoyl chlorides with tributyltin radicals are the β-scission product (nitrile) and the product resulting from hydrogen atom abstraction (imine), suggesting competitive pathways.[6h] It must be noted that the yields were found to be dependent on the temperature and the concentration of tributyltin hydride in the addition mixture, however, with the exception of one substrate, products from β-scission and from hydrogen atom abstraction were formed in every single case. On the basis of these results, we would expect that, under similar conditions,

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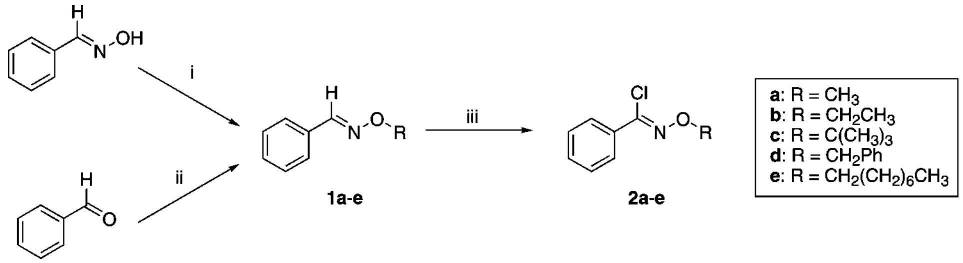
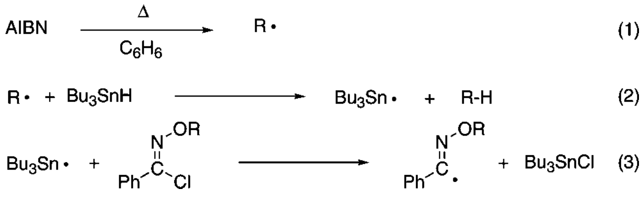


FIGURE 1. Preparation and structure of the *N*-Alkoxybenziminoyl chlorides (**2**) used in this study. (i) NaOH, $C_8H_{17}Br$, solvent, reflux; (ii) H_2N OR HCL, NaOH, EtOH, reflux; (iii) NCS, DMF.

SCHEME 6. Reaction Scheme for the Generation of *N*-Alkoxybenziminoyl Radicals



the generation of *N*-alkoximinoyl radicals will result in the formation of both nitriles (β-scission) and oxime ethers (hydrogen abstraction). Interestingly, no kinetic studies have been carried out on reactions involving iminoyl radicals, nor have there been any systematic studies on the reactivity of *N*-alkoximinoyl radicals, thereby limiting their use in synthetic applications.

To further investigate the involvement of *N*-alkoxybenziminoyl radicals in the formation of nitriles from aldoximes and aldoxime ethers and to learn about the reactivity of these reactive intermediates, we have used the known methodologies from studies on *N*-alkyliminoyl radicals to generate the radicals of interest. Here we present our results on the studies of these novel intermediates and report, for the first time, estimated rate constants for some of the observed reactions.

Results and Discussion

Product Formation in the Reactions of *N*-Alkoxybenziminoyl Radicals. Because *N*-alkoxybenziminoyl radicals have received little attention, we decided to generate these radicals via chlorine atom abstraction by the tributyltin radical. This method had been successfully used for the generation of *N*-alkyliminoyl radicals as described by Wirth and Rüchardt.[6h] The required *N*-alkoxybenziminoyl chlorides (**2a**−**e**; Figure 1) were prepared from the corresponding *O*-alkyl benzaldoximes (**1a**−**d**) via reaction with *N*-chlorosuccinimide (NCS) as reported by Howe.[7] Oxime ethers **1a**−**d** were prepared from reaction of benzaldehyde with the appropriate *O*-alkyl hydroxylamine hydrochloride salt.[3,5] Oxime **1e** was prepared from reaction of benzaldehyde oxime with sodium hydroxide, followed by addition of 1-bromooctane.

The desired *N*-alkoxybenziminoyl radicals were generated via reaction of the corresponding *N*-alkoxybenziminoyl chloride with tributyltin hydride and AIBN in refluxing benzene, according to reactions 1−3 in Scheme 6.[6h] The reactions were followed by gas chromatography and the products were identified by comparison to authentic standards. Blank experiments were done to make sure no reactions occurred in the injector port of the gas chromatograph. The experiments were carried out in the presence and absence of oxygen (air). The results of these studies are shown in Tables 1 and 2.

TABLE 1. Products and Percent Yields in the Thermal Reactions of *N*-Alkoxybenziminoyl Chlorides 2a−e in Argon-Purged Benzene in the Presence of AIBN (0.005 M) and Different Concentrations of Bu_3SnH

	conversion[a]	3[b]	4[c]	5[d]	1[e]
		0.025 M Bu_3SnH			
2a	71	74	–[f]	–[f]	<1[g]
2b	69	73	–[f]	–[f]	<1[g]
2c	51	77	–[f]	–[f]	<1[g]
2d	48	92	89	3	<1[g]
2e	73	100	92	7	<1[g]
		0.25 M Bu_3SnH			
2a	100	100	–[f]	–[f]	<1[g]
2b	100	100	–[f]	–[f]	<1[g]
2c	90	88	–[f]	–[f]	<1[g]
2d	100	76	69	1	<1[g]
2e	100	100	92	1	<1[g]

[a] Conversion of **2** determined by calibrated GC-FID. [b] Yield of benzonitrile. [c] Yield of alcohol (**4a**−**e**) product. [d] Amount of aldehyde (**5a**−**e**) product. [e] Amount of oxime ether (**1a**−**e**) product. [f] Products could not be detected by gas chromatography due to volatility. [g] Amount below the detection limit.

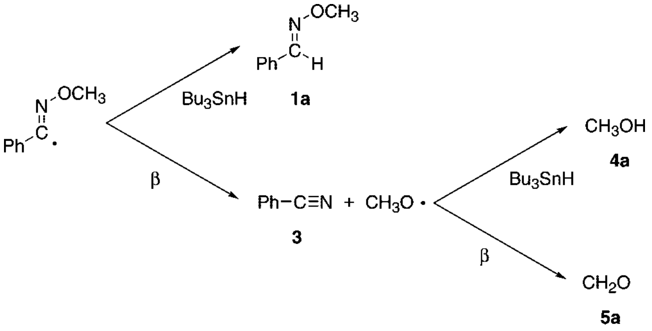
TABLE 2. Products and Percent Yields in the Thermal Reactions of *N*-Alkoxybenziminoyl Chlorides 2a−e in Air-Saturated Benzene in the Presence of AIBN (0.005 M) and Different Concentrations of Bu_3SnH

	conversion[a]	3[b]	4[c]	5[d]	1[e]
		0.025 M Bu_3SnH			
2a	75	100	–[f]	–[f]	<1[g]
2b	72	99	–[f]	–[f]	<1[g]
2c	57	91	–[f]	–[f]	<1[g]
2d	60	53	35	1	<1[g]
2e	74	80	76	4	<1[g]
		0.25 M Bu_3SnH			
2a	75	100	–[f]	–[f]	<1[g]
2b	100	100	–[f]	–[f]	<1[g]
2c	93	83	–[f]	–[f]	<1[g]
2d	96	95	51	1	<1[g]
2e	100	96	93	1	<1[g]

[a] Conversion of **2** determined by calibrated GC-FID. [b] Yield of benzonitrile. [c] Yield of alcohol (**4a**−**e**) product. [d] Amount of aldehyde (**5a**−**e**) product. [e] Amount of oxime ether (**1a**−**e**) product. [f] Products could not be detected by gas chromatography due to volatility. [g] Amount below the detection limit.

Reflux of an argon-purged solution of *N*-methoxybenziminoyl chloride (**2a**, 0.015 M), tributyltin hydride (0.025 M) and AIBN (0.005 M) in benzene for 1 h resulted in the formation of benzonitrile as the only product (Table 1). The expected product from the reduction pathway (*O*-methylbenzaldehyde oxime, **1a**) was not formed under these conditions (less than 1%). Attempts to trap the intermediate *N*-methoximinoyl radical by employing

SCHEME 7. Expected Products from Reactions of *N*-Methoxybenziminoyl Radicals



higher concentrations of Bu_3SnH (0.25 M) or by using toluene as the solvent were unsuccessful, suggesting that the β-scission pathway is a very efficient process. However, the other expected product(s) from the β-scission pathway (alcohol **4a** and aldehyde **5a**; Scheme 7) could not be detected by gas chromatography (due to volatility issues) and therefore it cannot be concluded (at this point) that this pathway actually takes place.

Similar results were obtained for *N*-ethoxybenziminoyl chloride (**2b**) and *N*-*t*-butoxybenziminoyl chloride (**2c**). Other than formation of benzonitrile, no direct evidence was found for the β-scission pathway, since the expected products from the radical fragment in these reactions (methanol, **4a**; formaldehyde, **5a**; ethanol, **4b**; acetaldehyde, **5b**; and *t*-butanol, **4c**, respectively) could not be identified with the available experimental techniques. However, using *N*-benzyloxybenziminoyl chloride (**2d**) under similar conditions led to the formation of benzonitrile (**3**), benzyl alcohol (**4d**) and benzaldehyde (**5d**). The latter two products confirm the suspected β-scission pathway. Similarly, reacting *N*-octyloxybenziminoyl chloride (**2e**) yielded benzonitrile (**3**), 1-octanol (**4e**) and octanal (**5e**) as expected. In general, the material balances in these experiments are acceptable. It is known that tin radicals can react with carbon−nitrogen double bonds,[9] which may explain the lower material balances for compounds **2a**−**c**. Analysis of the mixtures by GC-MS suggested the formation of some products containing tin (including tributyltin chloride and hexabutylditin), however these were not isolated or quantified.

Comparing these results to those obtained by Wirth and Rüchardt in their studies on *N*-alkyliminoyl radicals[6h] reveals some significant differences. The reaction of *N*-benzylbenziminoyl chloride in benzene resulted in the formation of benzonitrile (76.5%), toluene (74.4%) and *N*-benzylbenzaldimine (10.1%). Under similar conditions, *N*-octylbenziminoyl chloride reacted to give only 2.4% (each) of benzonitrile and octane and 93.6% of *N*-octylbenzaldimine. Other substrates (with the exception of *N*-cinnamylbenziminoyl chloride) also reacted to yield the imine product independent of the solvent (benzene, toluene, xylene) or concentration of Bu_3SnH, although the material balance often was poor. In a separate study, Bringmann, Barton and co-workers noted that reaction of an iminoyl chloride derivative of a steroid with Bu_3SnH resulted in the formation of benzylamine (64%), suggesting that β-scission was not a dominant pathway (Scheme 8).[10]

It is unclear why *N*-alkoximinoyl radicals react differently as compared to *N*-alkyliminoyl radicals. One possible scenario would be that oxime ethers are formed but react on under the conditions of the reaction to form the nitrile product (Scheme 9). To find out if these follow-up reactions were occurring, oxime ether **1d** was reacted with Bu_3SnH and AIBN in benzene under reflux. Although small amounts of benzonitrile were detected, the conversion of the oxime ether was at most 5%; therefore it can be concluded that this reaction is of no significance and cannot be used to explain the absence of the oxime ether in the product mixture. The most likely explanation at this point is that the β-scission pathway that leads to the formation of alkoxy radicals is energetically more favorable than that of similar alkyl radicals. This may simply be a result of a difference in bond dissociation energies; the N−O BDE in acetaldoxime is 49.7 kcal mol^{-1} whereas the typical C−N BDE is upward of 70 kcal mol^{-1}.[11,12]

When the reactions were carried out in air-saturated benzene the results were very similar to those in the argon-purged solutions (Table 2). Again, all compounds give good (~80%) to excellent (~100%) material balances with the exception of **2d**. The reason for this behavior is unclear; the results are different in the absence and in the presence of air, which suggests that it may be due to follow up reactions with oxygen although it is unclear why only one of these substrates would be susceptible to this effect. At this point we have not further investigated this behavior.

Estimation of the Rate Constants for *β*-Scission in *N*-Alkoxybenziminoyl Radicals. On the basis of the results listed in Tables 1 and 2, it can be concluded that *N*-alkoxybenziminoyl radicals undergo a β-scission to yield benzonitrile and an alkoxy radical. Since the product from the reduction pathway (hydrogen atom transfer, HAT, from Bu_3SnH) is not observed, it seems reasonable to assume that the β-scission pathway is significantly faster than the HAT pathway. Since there are no reports on the rate constant for either the hydrogen atom transfer or the β-scission reactions in iminoyl radicals, we have attempted to use our data together with some literature sources for an estimate of these numbers.

First, it must be noted that the product formation (products and yields) is unaffected by the presence of oxygen. The reactions of carbon-centered radicals with oxygen in solution vary from 10^6 to 10^9 M^{-1} s^{-1};[13,14] the "slow" reactions are observed for stabilized radicals (e.g., benzylic) although other resonance stabilized radicals have rate constants of $2 - 3 \times 10^8$ M^{-1} s^{-1}.[13] A fast reaction of the *N*-alkoxybenziminoyl radical with oxygen (k_{Ox}) would be competitive with the β-scission pathway and it would likely lead to different products or a diminished material balance. However, as seen from Tables 1 and 2, the material balances do not change significantly when

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[10] Barton, D. H. R.; Bringmann, G.; Lamotte, G. *Tetrahedron Lett.* **1979**, *24*, 2291.

[11] Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, FL, 2003.

[12] Although the BDE of the C−N bond in a typical imine is unknown, a survey of different C−N BDE values suggest that most are in the range of 70−100 kcal mol^{-1}.[11]

[13] For a listing of rate constants for the reactions of carbon-centered radicals with O_2 see: (a) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1990**, *19*, 413. (b) Howard, J. A.; Scaiano, J. C. In *Landolt-Barnstein Numerical Data and Functional Relationships in Science and Technology. New Series, Group ll; Atomic and Molecular Physics*; Hellwege, K.-H., Madelung, O., Eds.; Springer-Verlag: Berlin, 1984; Vol. 13, Part d.

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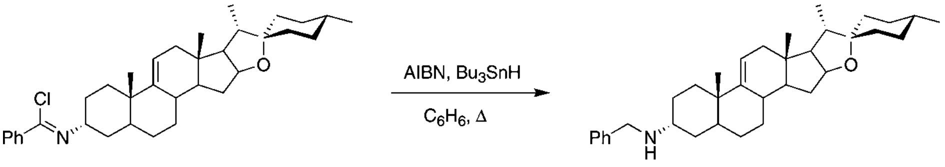
SCHEME 8. Reduction by Tributyltin Hydride of the Steroid Derivative of a Benziminoyl Chloride[10]



SCHEME 9. Possible Alternative Pathway for Product Formation in the Reactions of *N*-Alkoxybenziminoyl Chlorides

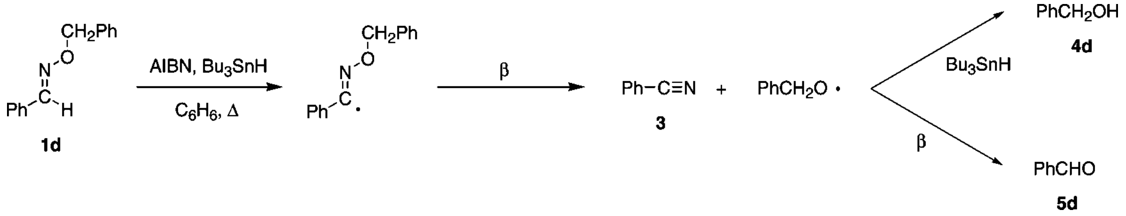
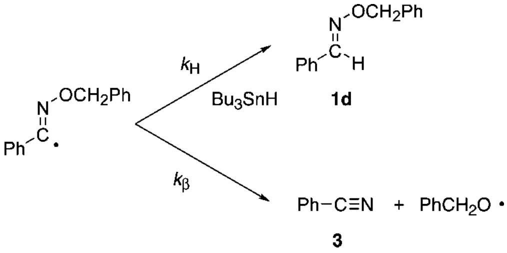


TABLE 3. Summary of Literature Rate Constants for Solution-Phase Reactions of sp^2-Hybridized Carbon-Centered Radicals with Oxygen and Tributyltin Hydride

entry	reaction	rate constant (M^{-1} s^{-1})	reference
1	$C_6H_5^• + O_2 \rightarrow C_6H_5OO^•$	7.1×10^8	14b
2	$C_6H_5^• + O_2 \rightarrow C_6H_5OO^•$	4.6×10^9	14c
3	$^-O_2C{-}C_6H_5^• + O_2 \rightarrow {}^-O_2C{-}C_6H_5OO^•$	1.6×10^9	14b
4	$C_6H_5C(O)^• + O_2 \rightarrow C_6H_5C(O)OO^•$	1.8×10^9	14d
5	$H_2C{=}CH^• + O_2 \rightarrow H_2C{=}CHOO^•$	4.6×10^9	14c
6	$C_6H_5^• + Bu_3SnH \rightarrow C_6H_6 + Bu_3Sn^•$	7.8×10^8	16d
7	$(CH_3)_3C(O)^• + Bu_3SnH \rightarrow (CH_3)_3CHO + Bu_3Sn^•$	3.9×10^5	16b,c
8	$(CH_3)_2C{=}CH^• + Bu_3SnH \rightarrow (CH_3)_2C{=}CH_2 + Bu_3Sn^•$	3.5×10^8	16a

changing from an argon-purged solution to an air-saturated solution. This suggests that the β-scission pathway is faster than reaction of the *N*-alkoximinoyl radicals with oxygen. The rate constant for the reaction of an sp^2-hybridized carbon radical with oxygen can be estimated from available literature values (Table 3, entries 1−5). For example, the reaction of the phenyl radical with oxygen (in water) has a reported rate constant of 3.8×10^9 M^{-1} s^{-1},[14a] although it has been suggested that this report used an incorrect O_2 concentration.[14b] A value corrected for the O_2 concentration is 7.1×10^8 M^{-1} s^{-1}. Mertens and von Sonntag[14c] measured a value of 4.6×10^9 M^{-1} s^{-1} for the same reaction and Neta and co-workers reported a value of 1.6×10^9 M^{-1} s^{-1} for the reaction of 4-carboxyphenyl radical with oxygen.[14b] Other known solution-phase rate constants for the reaction of sp^2-carbon centered radicals with oxygen are also on the order of 10^9 M^{-1} s^{-1} (e.g., benzoyl radical, 1.8×10^9 M^{-1} s^{-1};[14c] ethenyl radical, 6.4×10^9 M^{-1} s^{-1}).[14d] On the basis of these values, it seems reasonable to assume a similar rate constant for the reaction of an iminoyl radical with oxygen. Using a rate constant, k_{Ox}, of 1.0×10^9 M^{-1} s^{-1} for the reaction of an sp^2-hybridized carbon centered radical with oxygen and assuming that the benzene solution is saturated with air (0.21 atm O_2; $[O_2] = 1.9 \times 10^{-3}$ M),[15] we can estimate the rate of the reaction of *N*-alkoxybenziminoyl radicals with oxygen to be approximately 1.9×10^6 s^{-1}. Therefore, if the rate constant of β-scission (k_β) is approximately 2×10^6 s^{-1} or slower, we would expect to see a significant effect from the presence of oxygen. Since no such effect is observed we can conclude that k_β must be significantly greater than 10^6 s^{-1}.

SCHEME 10. Possible Follow-up Reactions for *N*-Alkoxybenziminoyl Radicals



To determine the rate constant for the β-scission pathway (k_β) of the intermediate *N*-alkoxybenziminoyl radicals we needed a value for the hydrogen atom abstraction pathway. Unfortunately, the rate constant for this pathway (k_H) has not yet been determined, and therefore we have to rely on the measured rate constants for similar reactions. Several rate constants for the reactions of different sp^2-hybridized carbon-centered radicals with Bu_3SnH have been determined experimentally (Table 3, entries 6 − 8). The rate constants vary from anywhere between 10^5 and 10^8 M^{-1} s^{-1}, depending on the structure of the radical.[16] For our purposes, we have chosen a rate constant of 1×10^6 M^{-1} s^{-1} as a lower limit for this process.

Now that we have established a lower limit for the HAT process we can estimate a rate constant for the β-scission pathways. Using the reaction of iminoyl chloride **2d** (Scheme 10) as an example it can be seen that the two competing pathways for the *N*-alkoxybenziminoyl radicals are hydrogen atom transfer to yield the oxime ether **1** (k_H) and β-scission to yield benzonitrile **3** (k_β). Because both products are directly formed directly from the same intermediate, we can use the

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(15) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Dekker: New York, 1993.

(16) (a) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594. (b) Chatgilialoglu, C.; Lucarini, M. *Tetrahedron Lett.* **1995**, *36*, 1299. (c) Chatgilialoglu, C.; Ferreri, C.; Lucarini, M.; Pedrielli, P.; Pedulli, G. F. *Organometallics* **1995**, *14*, 2672. (d) Garden, S. J.; Avila, D. V.; Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U.; Lusztyk, J. *J. Org. Chem.* **1996**, *61*, 805.

product ratio to determine the approximate rate constants for each pathway:

$$\frac{[\mathbf{1d}]}{[\mathbf{3}]} = \frac{k_{\mathrm{H}}[\mathrm{Bu_3SnH}]}{k_\beta}$$

which can be rewritten as:

$$k_\beta = \frac{k_{\mathrm{H}}[\mathrm{Bu_3SnH}][\mathbf{3}]}{[\mathbf{1d}]}$$

Using $k_{\mathrm{H}} = 1 \times 10^6$ $\mathrm{M^{-1}\ s^{-1}}$ and $[\mathrm{Bu_3SnH}] = 0.25$ M we obtain a value of 2.5×10^5 $\mathrm{s^{-1}}$ for k_β if the product ratio {**1d**/**3**} is equal to 1. Since the product from the hydrogen atom abstraction pathway (oxime ether **1d**) was not detected (less than 1% yield, i.e., {**3**/**1d**} > 1×10^2), the lower limit for the rate constant for the β-scission process in *N*-alkoxybenziminoyl radicals is estimated to be greater than 2.5×10^7 $\mathrm{s^{-1}}$. This is in agreement with the estimate presented above which suggests that the rate of β-scission is significantly greater than 10^6 $\mathrm{s^{-1}}$. If k_{H} is in the range of 10^8 $\mathrm{M^{-1}\ s^{-1}}$ (similar to the reactions of phenyl radical and isobutenyl radical),[16a,b] the rate constant for β-scission will be on the order of 2.5×10^9 $\mathrm{s^{-1}}$.

Conclusions

Generation of *N*-alkoxybenziminoyl radicals from the corresponding *N*-alkoxybenziminoyl chlorides by means of the tributyltin radicals results in a rapid and highly efficient β-scission process, which yields the nitrile and the alkoxy radical. The β-scission pathway is too fast for hydrogen atom abstraction to compete. Using an estimated rate constant of 1×10^6 $\mathrm{M^{-1}s^{-1}}$ for the hydrogen atom abstraction process (k_{H}), the lower limit for the rate constant for the β-scission process (k_β) is estimated to be 2.5×10^7 $\mathrm{s^{-1}}$. The reactivity of *N*-alkoximinoyl radicals is different than that of the similar *N*-alkyliminoyl radicals, which react to give both products from reduction and β-scission. The difference is thought to be a result of different bond strengths (cleavage of the N−O bond versus the N−C bond), although more evidence is expected to come from theoretical studies on these intermediates. These results seem to confirm the formation of alkoximinoyl radicals in the photooxidation of aldoximes as shown by the formation of the corresponding nitriles. In addition, the use of *N*-alkoxybenziminoyl chlorides is a novel and highly efficient method for the generation of alkoxyl radicals in solution. Further work is underway to determine the exact rate constants for the β-scission processes in iminoyl radicals.

Experimental Section

Materials. All chemicals other than the aldoxime ethers (**1**) and the benziminoyl chlorides (**2**) were commercially available and were used without further purification. The aldoxime ethers were prepared from benzaldehyde and commercially available *O*-alkylhydroxylamine hydrochloride salts or from reaction of benzaldehyde oxime with the appropriate alkyl halide in the presence of base (see below). Benzene (spectrophotometric grade) was used as received.

Thermal Reactions. The desired *N*-alkoxybenziminoyl radicals were generated via reaction of the corresponding *N*-alkoxybenziminoyl chloride (**2**) with tributyltin hydride and AIBN in refluxing benzene. In a typical experiment, a 25 mL round-bottom flask was charged with the appropriate *N*-alkoxybenziminoyl chloride (**2**, 0.015 M), tributyltin hydride (0.025 or 0.25 M) and AIBN (0.005 M). Benzene (10 mL) was added and the mixture was refluxed for 1 h. Afterward, the reaction mixture was analyzed by gas chromatography and the products were identified by comparison to authentic standards. Blank experiments were done to make sure no reactions occurred in the injector port of the gas chromatograph. The experiments were carried out in the presence and absence of oxygen (air).

Synthesis of *O*-Alkyl Benzaldehyde Oximes. The preparations of oxime ethers **1a**−**d** have been reported previously.[5] In general, the oxime ethers were prepared by the addition of the appropriate *O*-alkyl hydroxylamine hydrochloride and a few drops of concentrated hydrochloric acid to benzaldehyde in 95% ethanol (50 mL). The mixture was refluxed for 2−6 h after which the solvent was removed under reduced pressure. The crude product (oil) was purified by column chromatography using a hexane−ether gradient.

Synthesis of *N*-Alkoxybenziminoyl Chlorides (2a−**e).** The synthesis of the *N*-alkoxylbenziminoyl chlorides was accomplished using a modification of the procedure by Howe.[7] A 10 mL round-bottom flask was charged with the appropriate *O*-alkyl benzaldehyde oxime (0.006 mol) and DMF (5.0 mL). While stirring the solution, *N*-chlorosuccinimide (NCS, 0.006 mol) was slowly added. After the addition was complete the mixture was stirred for 48 h. Afterward the solution was poured into ice water (20 mL) and the resulting mixture was extracted three times with dichloromethane. The combined organic layers were dried over magnesium sulfate and after filtration the solvent was removed under reduced pressure yielding an oily residue. The iminoyl chlorides were further purified by column chromatography on silica gel using a hexane-ethyl acetate gradient.

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Supporting Information Available: Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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