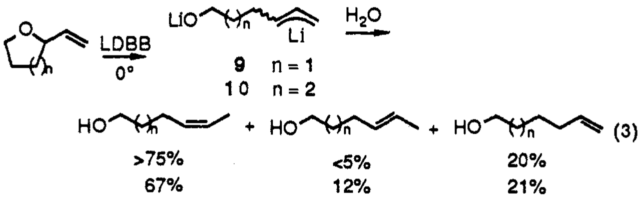
indicates the relative rates of BF_3-induced reductive cleavage of the C–O bonds of THFs with different degrees of 2-substitution. They were determined by using large excesses of equimolar quantities of THF and substituted THF followed by protonation of the generated dianions and GC estimation of the alcohols (80–90% yields) produced. In due course, we shall report our success in reversing the regiochemistry of reductive lithiation of substituted oxetanes[2] by the use of Lewis acids.

We then sought a solvent in which lithium radical anions can be generated but which is not reductively cleaved in the presence of BF_3 so that an expansion of this method to a wider variety of THFs would be possible. To date, a lithium biphenylide–dimethyl ether system has provided the best results,[12] and we were able to isolate the coupling product from the reaction of isobutyraldehyde with our model dianion derived from 2,2-dimethyltetrahydrofuran in a modest 42% yield.

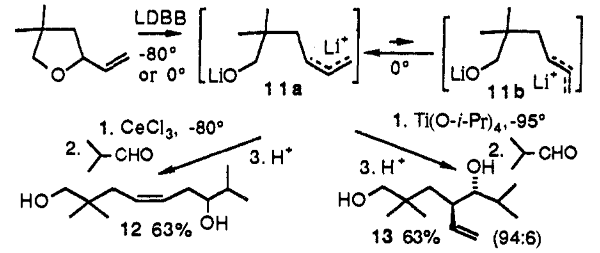
The second method of lowering the energy of the THF LUMO and stabilizing the open-chain radical anion is to append an alkenyl group to the 2-position of the ring. We reasoned that π^* orbitals are lower in energy than σ^* orbitals, that bond rotations would allow the π^* orbital to become parallel to the C–O bond that was cleaving, and that allylic resonance would stabilize the ring-cleaved radical. Encouraging precedents were the reductive cleavage of 4-phenyl-1,3-dioxanes[13] and the production of benzyllithium by reductive lithiation of benzyl ethyl ether.[14,15]

The starting materials were synthesized in 50–70% yield either by employing the previously reported[2] one-pot procedure involving the addition of γ-lithioalkoxides (generated from oxetanes) to α,β-unsaturated carbonyl compounds followed by acid-induced ring closure of the resulting 1,4-diols,[16] or by treating 2-bromotetrahydrofuran or 2-bromotetrahydropyran with vinylmagnesium bromide.[17] The reductive cleavages of 2-vinyltetrahydrofuran and 2-vinyltetrahydropyran by LDBB in THF were rapid at 0 °C and produced the corresponding terminal oxyallylic dianions **9** and **10**. In both cases the major isolated product after protonation was the (*Z*)-alkenyl alcohol (eq 3), reflecting the predominant existence of terminal *cis*-allyllithiums in THF under thermodynamic conditions.[18a]

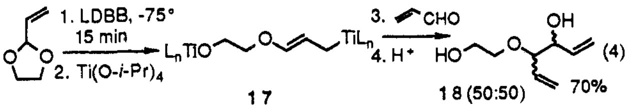


Techniques recently reported from this laboratory[18] can be used to attain excellent regiochemical and stereochemical control in reactions of isobutyraldehyde with the dianion **11** resulting from reductive cleavage of 4,4-dimethyl-2-vinyltetrahydrofuran. Thus, transmetalation with $CeCl_3$ resulted overwelmingly (98.7:1.3) in reaction at the least substituted allylic terminus, providing the cis olefin **12** and only a trace of the trans isomer. Alternatively, the use of titanium isopropoxide gave very largely (regiochemical control 89:11) **13** resulting from attack on the other terminus; as expected,[19] the intermediate *trans*-allyltitanium, with the bulky metal σ-bound to the least substituted terminus, resulted in an almost completely anti configuration of **13** (Scheme IV). The somewhat similar results obtained with other 2-vinyltetrahydrofurans will be chronicled in the full paper.

Scheme IV



Preliminary experiments indicate that some cyclic ethylene acetals of enals can also be reductively lithiated by LDBB in THF. The resulting α-alkoxyallyl systems, after transmetalation with Ti^{IV} and trapping with α,β-unsaturated aldehydes and ketones, yield 4-alkoxy 1,5-dien-3-ols such as **18** (e.g., eq 4), starting materials for the anionic oxy-Cope rearrangement.[20]



Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Sample procedures for generation of δ-lithioalkoxides and terminal oxyallylic dianions and for their reactions with electrophiles and the spectral data of the products (3 pages). Ordering information is given on any current masthead page.

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(12) Solutions of LDBB, 0.2 M, could sometimes be generated in dry, deoxygenated DME under ultrasonication, but the reproducibility of this process was low; reactions of lithium and DBB in tetrahydropyran were sluggish and stopped at ≅20% conversion.

(13) Bailey, W. F.; Cioffi, E. A. *J. Chem. Soc., Chem. Commun.* **1981**, 155.

(14) Gilman, H.; Schwebke, G. L. *J. Org. Chem.* **1962**, *27*, 4259.

(15) Review of reductive ether cleavages; Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *36*, 972.

(16) In reactions involving acrolein, γ-cerioalkoxides gave better yields.

(17) Ficini, J. *Bull. Soc. Chim. Fr.* **1956**, 122.

(18) (a) Guo, B.-S.; Doubleday, W.; Cohen, T. *J. Am. Chem. Soc.* **1987**, *109*, 4710 and citations therein. (b) Cohen, T.; Guo, B.-S. *Tetrahedron* **1986**, *42*, 2803.

(19) Reetz, M. T.; Steinbach, R.; Westermann, J.; Peter, R.; Wenderoth, B. *Chem. Ber.* **1985**, *118*, 1441 and citations therein.

(20) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *J. Am. Chem. Soc.* **1978**, *100*, 2242.

Kinetic and Thermodynamic Stability of α-Azidobenzyl Carbocations: Putative Intermediates in the Schmidt Reaction

Tina L. Amyes* and John P. Richard

Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506-0055

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We report here the first direct demonstration of the formation of α-azido-stabilized carbocations. The azido group is one of the most versatile functionalities in organic chemistry.[1] As a substituent it stabilizes developing positive or negative charge at an adjacent carbon and thereby accelerates both electrophilic and nucleophilic aromatic substitution reactions.[2] The thermodynamically favorable loss of nitrogen from the azido group drives several rearrangement reactions.[3] Azide ion is a good leaving group in S_N1 reactions[4] and also a reactive nucleophile for capture of carbocations.[5,6] Recent calculations predict that α-azido carbocations are highly stabilized by resonance electron donation

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(1) For a recent review of the synthetic applications of organoazides, see: Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 297–368.

(2) Biffin, M. E. C.; Miller, J.; Paul, D. B. In *The Chemistry of the Azido Group*; Patai, S., Ed.; Wiley-Interscience: New York, 1971; Chapter 4.

(3) Banthorpe, D. V., Chapter 7 of ref 2. Smith, P. A. S. In *Molecular Rearrangements*; de Mayo, P., Ed.; Wiley-Interscience: New York, 1963; Chapter 8.

(4) Amyes, T. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 7888–7900.

(5) Bunton, C. A.; Huang, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 3536–3544. Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4966–4971.

(6) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913–6914.

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Scheme I

$$\text{4-XArCH(N}_3)_2 \underset{k_{az}[N_3^-]}{\overset{k_{solv}}{\rightleftharpoons}} \text{4-XArCH(N}_3)^+ \xrightarrow{k_s}$$

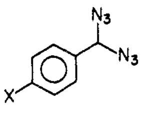
$$\text{4-XArCH(N}_3\text{)OH} \xrightarrow{fast} \text{4-XArCHO}$$

Table I. Rate and Equilibrium Constants for the Formation and Reaction of Ring-Substituted Benzyl Carbocations 4-XArCH(R)$^+$ Stabilized by an α-Azido and an α-Methoxy Group[a]

ring substituent X	α-substituent R	k_{solv}, s^{-1}	$K_{eq} = k_{solv}/k_{az}$,[b] M	k_s, s^{-1}
4-MeO	N_3	0.046	9×10^{-12}	3×10^5
	OMe[c]	0.72	1.4×10^{-10}	3×10^7
4-H	N_3	3.9×10^{-4}	8×10^{-14}	6×10^7
	OMe[d]	0.022	4.4×10^{-12}	2×10^9

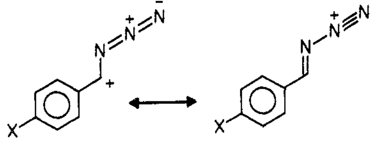
[a] At 25 °C, unless otherwise noted. Rate and equilibrium constants are as defined in Scheme I. Data for 4-MeO derivatives are for reaction in 50:50 (v/v) TFE/H_2O at ionic strength 0.50 ($NaClO_4$). Data for 4-H derivatives are for reaction in H_2O at ionic strength 2.0 ($NaClO_4$). [b] Calculated by using $k_{az} = 5 \times 10^9$ M^{-1} s^{-1}; see text. [c] Data from ref 14 and at 20 °C. [d] Data from ref 4.

from the α-azido group.[7] This suggests that α-azido carbocations (iminodiazonium ions) should be easily formed in aqueous solution[8] and that they might be sufficiently stable to serve as intermediates in the Schmidt reaction[3] of carbonyl compounds. We report rate and equilibrium constants for formation of the α-azido-stabilized benzyl carbocations **3** and **4**, generated in aqueous solutions as intermediates in the solvolysis of the corresponding *gem*-diazides **1** and **2**, and rate constants for reaction of **3** and **4** with solvent.



1 X = MeO

2 X = H



3 X = MeO

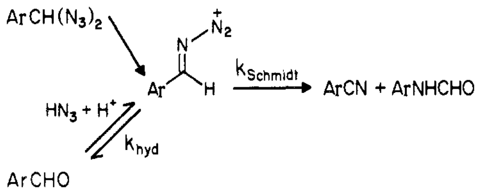
4 X = H

The observed rate constant for solvolysis of **1**[10] in 50:50 (v/v) trifluoroethanol/water decreased 300-fold as [NaN_3] was increased from 0 to 20 mM; at the lowest practical concentration of N_3^- (1 mM), the decrease was 20-fold. This common azide ion inhibition is direct evidence for solvolysis of **1** through the diffusionally equilibrated α-azido-4-methoxybenzyl carbocation (**3**) which is trapped by N_3^- to regenerate **1** or by solvent to yield, eventually, 4-methoxybenzaldehyde (Scheme I).[4,11] The values of k_{obsd} were fit by least-squares analysis to eq 1, derived for Scheme I, which gave $k_{az}/k_s = 15000$ M^{-1} for partitioning of **3** between reaction with N_3^- and with solvent. Similarly, the

$$k_{solv}/k_{obsd} = 1 + (k_{az}/k_s)[N_3^-] \qquad (1)$$

solvolysis of **2** in water is 50% inhibited by 0.011 M N_3^-, and k_{az}/k_s = 90 M^{-1} for partitioning of **4**. The reaction of N_3^- with benzyl carbocations is diffusion limited, with $k_{az} \approx 5 \times 10^9$ M^{-1} s^{-1},[6] and this serves as a "clock" for the reaction of solvent.[4,12,13] This value for k_{az} was used to calculate equilibrium constants for formation of **3** and **4** from **1** and **2** as $K_{eq} = k_{solv}/k_{az}$ (M), and rate constants for reaction of **3** and **4** with solvent, k_s (s^{-1}), from the partitioning ratio k_{az}/k_s.[4] These and literature data for α-methoxybenzyl derivatives are given in Table I.

Scheme II



The data show that **3** and **4** are thermodynamically *less stable* (16-fold and 60-fold, respectively) than the corresponding oxocarbenium ions, relative to the azide ion adducts. However, calculations predict that the α-azido methyl carbocation should be *more stable* than the α-hydroxy methyl carbocation in the gas phase.[7] These results may be explained by greater stabilization by a methoxy compared with a hydroxy group in the gas phase, and/or by the effect of the polar, largely aqueous, solvent, which would be expected to provide greater stabilization of the less delocalized oxocarbenium ions than of **3** and **4**.

There is the same absence of a correlation between the thermodynamic stability of α-substituted benzyl carbocations ($K_{eq} = k_{solv}/k_{az}$) and their kinetic stability (k_s) noted previously (Table I).[12b,13,14] The values of K_{eq} for formation of **3** and **4** from the azide ion adducts are 16-fold and 60-fold *smaller*, respectively, than those for formation of the respective oxocarbenium ions. However, capture of **3** by solvent is 100-fold *slower* than capture of the *more stable* carbocation 4-MeOArCH(OMe)$^+$. Similarly, reaction of **4** with water is ~30-fold slower than that of PhCH(OMe)$^+$.

These results are consistent with our proposal[14] that the effect of α-substituents on the reactivity of benzyl carbocations toward solvent is a result of effects on both the thermodynamic driving force and the intrinsic kinetic barrier for the reaction. The intrinsic barrier is related to the amount of electronic and structural reorganization that occurs upon movement from the ground to the transition state for the reaction.[15] The α-azido and α-methoxy groups both stabilize benzylic carbocations, by promoting resonance delocalization of the positive charge onto the terminal diazo group[7,16] or the α-oxygen, respectively. A simple explanation for the larger kinetic barrier for the capture of the α-azido compared with the α-methoxy carbocations is that the requirement for the loss of this resonance interaction at the transition state[17] for reaction with solvent results in a larger intrinsic barrier for reaction of the former. The loss of the resonance delocalization in **3** and **4** requires extensive electronic reorganization and structural change at three nitrogen atoms, but for α-methoxy carbocations these charges involve fewer atoms and bonds and are expected to lead to lower intrinsic barriers.

The Schmidt reaction of benzaldehydes with HN_3 in strongly acidic media gives mainly benzonitriles along with some formanilides (Scheme II).[3,18] Several intermediates, including α-azido carbocations, have been proposed for this reaction,[3] but little is known of their chemical and kinetic competence. This work represents the direct demonstration of the formation of one of these

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(7) Hoz, S.; Wolk, J. L. *Tetrahedron Lett.* **1990**, *31*, 4085–4088.

(8) α-Azido carbocations are predicted to be more stable than α-hydroxy carbocations,[7] and oxocarbenium ions (α-methoxy carbocations) derived from acetophenones,[9] benzaldehydes,[4] and aliphatic ketones[4] are easily formed in aqueous solution.

(9) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238–8248.

(10) **1** and **2** were prepared by reaction of the corresponding benzaldehydes with Me_3SiN_3 in CH_2Cl_2 with $SnCl_2$ as a catalyst: Nishiyama, K.; Oba, M.; Watanabe, A. *Tetrahedron* **1987**, *43*, 693–700. Workup by passage down a column of basic alumina, careful evaporation, and purification by column chromatography on silica gel gave the diazides in 88% yield. **CAUTION!** These compounds are explosive: Barash, L.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 3931–3932.

(11) UV spectroscopy and HPLC analysis showed that ≥90% of the products arise from reaction of **3** with water, rather than the less nucleophilic trifluoroethanol.

(12) (a) Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361–1372. (b) Richard, J. P.; Amyes, T. L.; Bei, L.; Stubblefield, V. *J. Am. Chem. Soc.* **1990**, *112*, 9513–9519.

(13) Richard, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 1455–1465.

(14) Amyes, T. L.; Richard, J. P. *J. Chem. Soc., Chem. Commun.*, in press.

(15) Bernasconi, C. F. *Tetrahedron* **1985**, *41*, 3219–3234.

(16) Bach, R. D.; Wolber, G. J. *J. Org. Chem.* **1982**, *47*, 239–245.

(17) There is good evidence that resonance interactions are lost to a greater extent than inductive interactions upon moving from the ground to the transition state for the reaction of benzyl carbocations[12-14] and oxocarbenium ions[4,9] with solvent.

(18) Schmidt, K. F. German Patent 427, 858, April 20, 1926. McEwen, W. E.; Conrad, W. E.; Van der Werf, C. A. *J. Am. Chem. Soc.* **1952**, *74*, 1168–1171.

putative intermediates in solution. Rearrangement or elimination with loss of nitrogen from **3** and **4** does not occur under our solvolysis conditions.[19] Therefore, if these α-azido carbocations *are* intermediates in the Schmidt reaction, then, under neutral solvolysis conditions, the reaction of water with **3** and **4** to give the benzaldehydes **1** and **2** is much faster than the step(s) which give the Schmidt-type products ($k_{\text{hyd}} \gg k_{\text{Schmidt}}$).

We conclude that if the Schmidt reaction proceeds through iminodiazonium ions, then either their formation from carbonyl compounds is reversible in concentrated acid or the decrease in the activity of water in these solutions leads to a change in rate-determining step, so that $k_{\text{Schmidt}} \gg k_{\text{hyd}}$.[20] Calculations suggest that equilibration of the cis and trans isomers of iminodiazonium ions cannot proceed by inversion at nitrogen, but must involve reversible hydration of the iminodiazonium ion to give the azidohydrin, followed by dehydration to give the geometrical isomer.[16]

Acknowledgment. We acknowledge National Institutes of Health Grant GM 39754 for support of this work.

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(19) Within the limits of detection, the reactions of **1** and **2** were shown by UV spectroscopy and HPLC analysis to give only the corresponding benzaldehydes.[11]

(20) The reactivities of oxocarbenium ions toward water in 60% and 90% sulfuric acid are ~10^4- and ~10^{10}-fold lower, respectively, than in dilute aqueous solution: McClelland, R. A.; Ahmad, M. *J. Am. Chem. Soc.* **1978**, *100*, 7031–7036.

First Direct Detection of Transient Organic Free Radicals in Solution by Time-Resolved Infrared Spectroscopy. Kinetic Studies on Some Acyl Radicals[1]

A. G. Neville,[2] C. E. Brown,[2] D. M. Rayner, J. Lusztyk, and K. U. Ingold*

Steacie Institute for Molecular Sciences
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6

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Acyl radical chemistry is an extremely active field at present,[3] but both absolute reactivities[4] and C=O stretching frequencies[6] of these species have been virtually unexplored in solution. Appropriate kinetic data would be of immeasurable value to synthetic chemists designing new radical chain reactions. However, it would not be easy to apply conventional laser flash photolytic (LFP) techniques since acyl radicals such as, for example, the benzoyl radical[3b,c] have only a weak absorption in the UV and this absorption occurs in the same wavelength range as absorptions from many other transient species. We have overcome these difficulties by a novel application of LFP using time-resolved infrared (TRIR) studies to detect and monitor some representative acyl radicals, $RC^{\bullet}{=}O$, in solution. This work represents the first direct observation of a transient organic free radical in solution by LFP/TRIR.[10]

Table I. LFP/TRIR Generation and Identification of Some Acyl Radicals

ketone	acyl radical	$\nu_{C=O}$,[a] cm^{-1}
$CH_3CH_2COCH_2C_6H_5$	$CH_3CH_2C^{\bullet}{=}O$	1859
$(CH_3)_2CHCOCH(CH_3)_2$	$(CH_3)_2CHC^{\bullet}{=}O$	1853
$(CH_3)_3CCOC(CH_3)_3$	$(CH_3)_3CC^{\bullet}{=}O$	1848
$C_6H_5COC(CH_3)_3$	$C_6H_5C^{\bullet}{=}O$	1828

[a] Estimated peak position. Error ±2 cm^{-1}.

Table II. Kinetic Data for Some Benzoyl Radical Reactions at Room Temperature (24 ± 1 °C)

quencher	product	k, M^{-1} s^{-1}
CCl_4	$C_6H_5C(O)Cl$	5.6×10^4
CCl_3Br	$C_6H_5C(O)Br$	2.2×10^8
C_6H_5SH	C_6H_5CHO	4.7×10^7

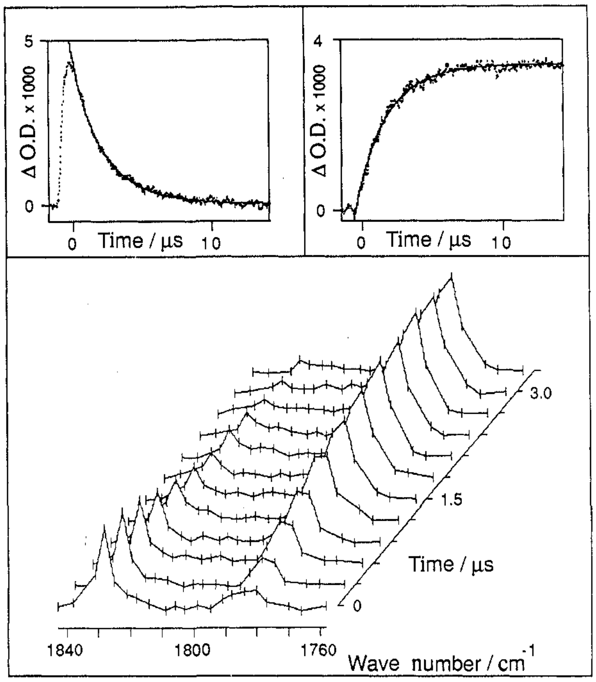

Figure 1. Time-resolved IR spectrum recorded during reaction of the benzoyl radical with 0.003 M CCl_3Br. Top left insert shows decay of the 1828-cm^{-1} band (benzoyl), and top right insert shows the growing in of the 1780-cm^{-1} band (benzoyl bromide) which was monitored at 1784 cm^{-1}.

The acyl radicals were generated by 308-nm LFP induced α-cleavage of appropriate ketones,[11] reaction 1, in Ar-saturated *n*-hexane as solvent using a calcium fluoride cell and a flow system at room temperature.[12] From each ketone (see Table I), only

$$RCOR' \xrightarrow[308\ \text{nm}]{h\nu} RC^{\bullet}{=}O + R'^{\bullet} \qquad (1)$$

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(1) Issued as NRCC No. 32319.

(2) NRCC Research Associate, 1989–1990.

(3) For some recent examples, see: (a) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 4003–4008, 4008–4011. Crich, D.; Fortt, S. M. *Tetrahedron* **1989**, *45*, 6581–6598. Bachi, M. D.; Bosch, E. *Heterocycles* **1989**, *28*, 579–583. Bachi, M. D.; Denenmark, D. *Heterocycles* **1989**, *28*, 583–588. Mestre, F.; Tailhan, C.; Zard, S. Z. *Heterocycles* **1989**, *28*, 171–174. (b) Weir, D.; Ajayaghosh, A.; Muneer, M.; George, M. V. *J. Photochem. Photobiol., A: Chem.* **1990**, *52*, 425–437. (c) Fischer, H.; Baer, R.; Hany, R.; Verhoolen, I.; Walbiner, M. *J. Chem. Soc., Perkin Trans. 2* **1990**, 787–798.

(4) The only previously reported absolute rate constants for reaction of an acyl radical with a compound in solution are a value of 4.8×10^5 M^{-1} s^{-1} at 25 °C for pivaloyl addition to acrylonitrile (obtained by a steady-state EPR technique),[5] and a value of 2.0×10^8 M^{-1} s^{-1} for the reaction of benzoyl with oxygen (obtained by laser flash photolysis with UV–visible detection).[3b]

(5) Jent, F.; Paul, H.; Roduner, E.; Heming, M.; Fischer, H. *Int. J. Chem. Kinet.* **1986**, *18*, 1113–1122.

(6) IR data on related $RC^{\bullet}{=}O$ radicals appear to be limited to the gaseous phase (R = H, F) and to solid matrices (R = H, F, Cl, CH_3, HO).[7,8]

(7) (a) Jacox, M. E. *J. Phys. Chem. Ref. Data* **1984**, *13*, 945–1068. (b) See also: Jacox, M. E. *J. Chem. Phys.* **1988**, *88*, 4598–4607. Brown, J. M.; Dumper, K.; Lowe, R. S. *J. Mol. Spectrosc.* **1983**, *97*, 441–448. McKellar, A. R. W.; Burkholder, J. B.; Orlando, J. J.; Howard, C. J. *J. Mol. Spectrosc.* **1988**, *130*, 445–453.

(8) Values of $\nu_{C=O}$ are markedly dependent on the matrix, e.g., for $CH_3C^{\bullet}{=}O$, $\nu_{C=O}$ ranges from 1796 cm^{-1} in a CO_2 matrix[9] to 1842 and 1875 cm^{-1} in argon matrices.[7a]

(9) Bennett, J. E.; Graham, S. C.; Mile, B. *Spectrochim. Acta* **1973**, *29A*, 375–383.

(10) To date, only one family of transient organic molecules has been detected in solution by LFP/TRIR; see: Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092–8098. For the first study of organic free radical kinetics using LFP/TRIR, see: Neville, A. G.; Brown, C. E.; Rayner, D. M.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 9269–9270.

(11) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 13.2.

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