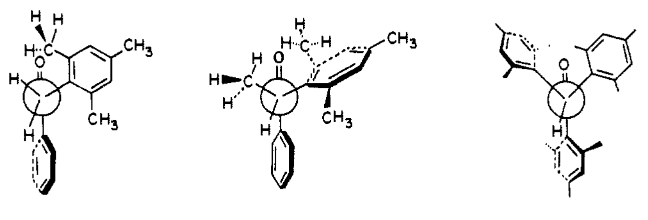
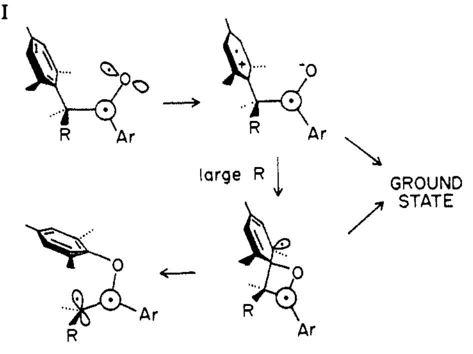
Chart I



2 **3** **1**

Scheme II



and coalesce at −38 °C; those for **5** coalesce below −80 °C. Line width analysis indicates a rotation rate of only 3000 s^{-1} for **3** and **4** at room temperature. The two separate ortho-methyls show chemical shifts of 1.9 and 2.6 ppm. The α-alkyl group obviously hinders bond rotation and forces the mesitylene ring to twist such that one ortho-methyl is held in the shielding region of the carbonyl, where it is not well positioned for hydrogen abstraction.[9] Thus the measured rate constant for this process is depressed. Chart I shows what are deduced to be the preferred conformations for **2** and **3**, the former from MMPMI calculations and precedent[10] (and the observed high reactivity), the latter from calculations and the NMR changes. The current results provide a unique example of how photoreactivity can be dominated by ground-state conformational preferences whenever bond rotations are significantly slower than excited-state decay reactions.[11]

The significant drop in triplet lifetime of **5** relative to **3**, together with the low yield of radicals, suggests that the process that initiates rearrangement to enol ether is both rapid and inefficient. This inefficiency is apparent even in **2**, where added Lewis base raises the indanol quantum yield from 0.44 to only 0.50. The inefficiency does *not* involve enol formation, since α-deuteriation does not affect the quantum efficiency of indanol formation from **2** and no H–D exchange occurs between the ortho-methyls and the α-carbon. In contrast, α-(2,4,6-triisopropylphenyl)acetophenone-α-d_2, which forms enol in high yield,[12] forms indanol in twice the quantum efficiency of the fully protonated compound and recovered starting ketone shows extensive D incorporation at an ortho-isopropyl group and H-incorporation at the α-carbon.

It appears that α-mesityl groups interact with n,π^* triplets in all the ketones studied; rate constants k_{CT} are included in Table I. We assume that the interaction is charge transfer in nature, as is alkylbenzene quenching of most triplet ketones,[13] and parallels the much faster quenching in β-phenyl ketones.[8b] Since mesitylene is a much better electron donor than is toluene, the effect does not show up in α-tolyl ketones.[3] The interaction leads to quenching in all cases but to enol ether only when the α-carbon is sufficiently crowded, as indicated in Scheme II. The preference for mesityl over phenyl migration in **5** probably reflects primarily a ground-state conformational preference[10,14] but would also be ensured by different donor abilities if free rotation occurred. The 1:1 Z/E enol ether ratios suggest that the rearrangement may represent a rare adiabatic triplet reaction. Certainly the near-orthogonal orientation of the half-occupied orbitals in the postulated biradical intermediate would more easily lead to triplet than to ground-state enol ether; and conversion of triplet ketone to triplet α-alkoxystyrene is exothermic.

The X-ray structure and NMR spectrum of **1**[14] (which gives only rearrangement) both indicate free rotation of both α-mesityl groups, with the preferred conformation shown in Chart I. This geometry should also allow fairly rapid δ-hydrogen abstraction. The fact that both indanol and enol ether arise from a triplet state of **5** with the same lifetime suggests that the competition between hydrogen abstraction and 1,3-shift may occur not in the triplet but in the CT complex, with the extent of steric congestion determining the partitioning. This question is under active investigation.

Acknowledgment. This work was supported by NSF Grant CHE-85-06703. We thank Prof. Zvi Rappoport for stimulating discussions.

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[9] Sheffer, J. R.; Dzakpasu *J. Am. Chem. Soc.* **1978**, *100*, 2163.

[10] Karabatsos, G. J.; Fenoglio, D. J. *Top. Stereochem.* **1970**, *5*, 167.

[11] (a) Lewis, F. D.; Johnson, R. W.; Johnson, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 6090. (b) Winnik, M. A. *Chem. Rev.* **1981**, *81*, 491. (c) Wagner, P. J. *Acc.Chem. Res.* **1983**, *16*, 461.

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[14] Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1007. Kaftory, M.; Biali, S. E.; Rappoport, Z. *Ibid.* **1985**, *107*, 1701.

[15] (a) Wagner, P. J.; McGrath, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 3849. (b) Lewis, F. D.; Magyar, J. G. *Ibid.* **1973**, *95*, 5973.

Nucleophile-Promoted Electrophilic Cyclization Reactions of Alkynes

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The participation of alkynes as nucleophiles in polyene cyclizations is well documented[1] notably through the extensive investigations of the Johnson group.[1,2] In contrast, cyclization reactions of alkynes with weak electrophiles such as iminium ions have received less attention.[3,4] In this communication we report that simple alkynes, although immune to reaction with intramolecular iminium ions in non-nucleophilic environments, cyclize readily with these versatile electrophiles in the presence of added nucleophiles.[5] We also report experiments that demonstrate that alkynes, although intrinsically less reactive than alkenes toward iminium cations, are dramatically more reactive than comparably substituted alkenes in cyclizations conducted in the presence of strong external nucleophiles.

Attempted cyclizations of the formaldiminium ion derived from 4-hexynylamine **1a** (5 equiv of paraformaldehyde, 1 equiv of camphorsulfonic acid, CH_3CN, 100 °C, 1 h) provided, upon quenching with aqueous base, only unchanged **1a** and the symmetrical diaminomethane derived from condensation of 2 equiv

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[1] For reviews, see: (a) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979; pp 123–147. (b) Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Chapter 5–6.

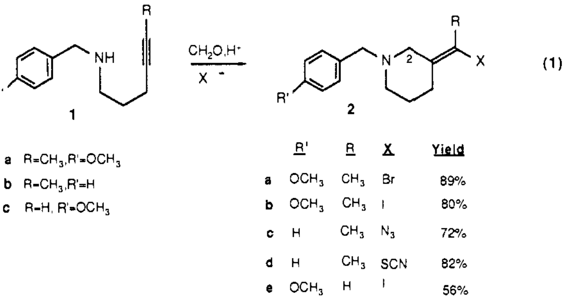
[2] (a) For a review, see: Johnson, W. S. *Bioorganic Chem.* **1976**, *5*, 51. (b) Johnson, W. S.; Ward, C. E.; Boots, S. G.; Gravestock, M. B.; Markezich, R. L.; McCarry, B. E.; Okorie, D. A.; Parry, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 88, and other papers in this series.

[3] We are aware of only a single example: Ahmad, V. U.; Feuerherd, K.-H.; Winterfeldt, E. *Chem. Ber.* **1977**, *110*, 3624.

[4] Several examples of intramolecular reactions of alkynes with more reactive *N*-acyliminium cations have been reported by Speckamp and coworkers; Dijkink, J.; Schoemaker, H. E.; Speckamp, W. N. *Tetrahedron Lett.* **1975**, 4043. Dijkink, J.; Speckamp, W. N. *Tetrahedron Lett.* **1975**, 4047. Boer-Terpstra, T.; Dijkink, J.; Schoemaker, H. E.; Speckamp, W. N. *Tetrahedron Lett.* **1977**, 939.

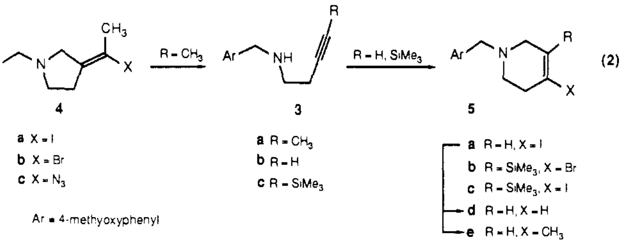
[5] For recent studies from our laboratories concerning the importance of added nucleophiles in determining the course of electrophilic cyclization reactions of alkenes, see: (a) McCann, S. F.; Overman, L. E. *J. Am. Chem. Soc.* **1987**, *109*, 6107. (b) McCann, S. F. Ph.D. Thesis, University of California, Irvine, 1987.

of **1a** with formaldehyde. However, identical treatment of **1a** in the presence of 5 equiv of tetra-*n*-butylammonium bromide afforded the exocyclic vinyl bromide **2a** in 90% yield.[6] Nucleophile-promoted cyclizations also can be carried out conveniently under aqueous conditions. For example, cyclizations[7a] of **1a** or **1b** in the presence of NaI (5 equiv, H_2O, 100 °C, 15 min), NaN_3 (30 equiv, 1:1 MeOH–H_2O, 75 °C, 3 h),[7c] or NaSCN (5 equiv, 1:1 MeOH–H_2O, 75 °C, 1.7 h) afforded vinyl iodide **2b** (80%), vinyl azide **2c** (72%), or vinyl thiocyanate **2d** (82%), respectively.[6] Attempted cyclizations[7b] of **1a** in the presence of weaker nucleophiles such as thiophenol or CH_3OH were less effective, the former yielding <15% of **2f** when employed as the solvent, while no cyclization was observed in CH_3OH.[8] On the other hand, even the less nucleophilic terminal alkyne **1c** was successfully cyclized[7b] in acetonitrile in the presence of tetra-*n*-butylammonium iodide (20 equiv, 82 °C, 2.8 h) to give **2e** in 56% yield.[6] To the limits of NMR detection at 500 MHz all the nucleophile-promoted cyclizations of **1** summarized in eq 1 were completely stereoselective.[10] The stereostructures of **2a–d** were easily established by observation of a large NOE enhancement between the vinyl methyl group and the C-2 methylene hydrogens (apparent singlet δ 3.0–3.16), while **2e** showed a corresponding strong NOE between the vinyl and the C-2 hydrogens.

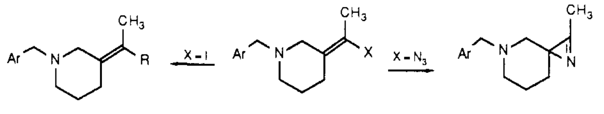


	R'	R	X	Yield
a	OCH_3	CH_3	Br	89%
b	OCH_3	CH_3	I	80%
c	H	CH_3	N_3	72%
d	H	CH_3	SCN	82%
e	OCH_3	H	I	56%
f	OCH_3	CH_3	SPh	<15%

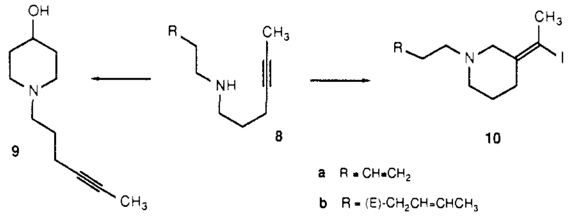
Cyclization of the 3-alkynylamines **3** addressed the question of the preferred mode (endo- or exocyclic) of ring closure[11] in nucleophile-assisted alkyne cyclizations. Cyclizations of the formaldiminium ion derived from **3a** occurred only in the exocyclic sense to afford the alkylidene pyrrolidines[6] **4a** (90%, 5 equiv of NaI, 100 °C, 15 min),[7a] **4b** (75%, 5 equiv of $(n\text{-Bu})_4NBr$, 82 °C, 1 h),[7b] and **4c** (45%, 30 equiv of NaN_3, 75 °C, 3 h).[7a] In marked contrast, iminium ion cyclizations of the terminal alkyne **3b** or the silylalkyne **3c** occurred predominantly in the endocyclic sense to afford the 1,2,5,6-tetrahydropyridines[6] **5a** (87%, 5 equiv of NaI, 100 °C, 1 h),[7a] **5b** (44%, 5 equiv of $(n\text{-Bu})_4NBr$, 100 °C, 4 h),[7b] and **5c** (60%, 5 equiv of $(n\text{-Bu})_4NI$, 82 °C, 1.5 h).[7b] The observed preference for closure in the exocyclic sense to form the five-membered ring product when the alkyne is not electronically biased parallels trends[1,2] observed in alkyne cyclizations carried out in the absence of strong nucleophiles.



The utility of these nucleophile-induced cyclization reactions in synthesis derives from the ready availability of alkynylamines[12] and the subsequent transformations that are possible by virtue of the vinylic functionality of the cyclization product. For example, treatment of **5a** with *n*-BuLi followed by protonolysis with MeOH gave tetrahydropyridine **5d** in 91% yield, while reaction of **5a** with $LiMe_2Cu$ afforded tetrahydropyridine **5e** in 76% yield.[6] Similar dehalogenations of the alkylidene piperidines **2a** and **2b** and alkylidene pyrrolidines **4a** and **4b** occurred with complete stereospecificity to afford the corresponding exocyclic trisubstituted alkenes (e.g., **2b** → **6a** in 74% yield, see eq 3). This sequence achieves a net reductive cyclization, in which the intramolecular iminium ion carbon and formally an external hydride are added in an antarafacial iminium ion carbon and formally an external hydride are added in an antarafacial fashion to the starting alkyne.[13] The vinyl halide functionality can also be utilized to elaborate, with complete stereocontrol, a tetrasubstituted double bond as exemplified by the conversion of **2b** → **6b** in 80% yield (*n*-BuLi; PhCHO), while the conversion to **2c** to the spiropiperidinyl azirine **7** (87%, thermolysis in refluxing toluene)[6] illustrates the opportunities provided by this new route to vinyl azides.



The pronounced sensitivity of alkynes to cyclization in the presence of nucleophiles is well-illustrated by conversions of the formaldiminium ions derived from **8a** and **8b** in which an alkyne and alkene compete as intramolecular nucleophiles.[15,16] Thus, while cyclization of **8a** in H_2O (2 equiv of formalin, 1 equiv of camphorsulfonic acid, 100 °C, 1 h) afforded the 4-hydroxypiperidine **9** in 73% yield (93% by GLC analysis), identical treatment of **8a** in the presence of 10 equiv of NaI afforded vinyl iodide **10a** in 76% yield as a result of **exclusive participation of the intramolecular alkyne nucleophile**.[6,17] The greater reactivity of an alkyne vis-a-vis an alkene in cyclizations conducted in the presence of added iodide was also observed in cyclizations[7a] of



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[6] Yields refer to isolated, purified product. Characterization data for key cyclization products are provided in the Supplementary Material. Structural assignments for **2a**, **2b**, **2e**, **4a**, **4b**, **5a**, **5b**, and **5c** were unambiguously established by chemical correlations.

[7] (a) Cyclizations in H_2O or H_2O–MeOH mixtures were carried out in the presence of excess formalin (2–30 equiv) and 1 equiv of camphorsulfonic acid. (b) Cyclizations in acetonitrile were carried out in the presence of 2–5 equiv of paraformaldehyde and 1 equiv of camphorsulfonic acid. (c) This reaction employed 5 equiv of camphorsulfonic acid. The yield was ca. 20% lower when 1 equiv of acid was employed.

[8] Our studies to date would indicate that nonbasic nucleophiles with nucleophilic constants[9] η-CH_3I > 5.8 are useful cyclization promoters.

[9] Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319.

[10] To our knowledge, this is the first demonstration that alkyne cyclizations that have no steric bias proceed with high anti stereoselectivity. Johnson and co-workers[2b] have seen anti stereoselectivity in alkyne cyclizations that form the steroid D ring.

[11] Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

[12] Readily available by simple aminolysis (65–85% yield) of the tosylate derivative of the corresponding commercially available alkynol.

[13] This sequence provides a nice complement to the stereocontrolled preparation of exocyclic alkenes via stereospecific cyclizations of vinylsilanes.[14] In most cases a simple alkynylamine will be more readily available than a stereodefined vinylsilane.

[14] For a review, see: Blumenkopf, T. D.; Overman, L. E. *Chem. Rev.* **1986**, *86*, 857. For a recent example not included in this review, see: Corey, E. J.; Seibel, W. L. *Tetrahedron Lett.* **1986**, *27*, 905.

[15] Competition experiments of this general type have recently been employed by us to determine the relative reactivities of a variety of nucleophilic cyclization terminators[5b] as well as explore medium effects on terminator reactivity.[5a]

[16] Alkenes and alkynes react with many electrophiles at comparable rates.[1a] Alkenes are more reactive than alkynes in cyclizations carried out in non-nucleophilic solvents with *N*-acyliminium ion initiators.[4]

[17] Hydroxypiperidine **9a** is not converted to **10** when resubmitted to the cyclization conditions in the presence of NaI, nor is **10** converted to **9a** in the absence of NaI.

8b (5 equiv of NaI, 100 °C, 1 h) which gave **10b**[6] as the sole cyclic product.

In summary, the possibility to tune the reactivity of alkynes by external nucleophiles opens up new opportunities for the use of this readily available functional group. Our ongoing studies aim at extending nucleophile-promoted alkyne cyclizations to other initiating cations and ring sizes as well as providing some definition of the mechanism[18] of these transformations.

Acknowledgment. This investigation was supported by NIH Grant HL-25854 and by Shared Instrument Grants from the National Science Foundation.

Supplementary Material Available: Experimental procedures and characterization data for representative cyclic products **2a–d**, **4a**, **5a**, **5c**, **6b**, 7, 9, and **10a** are provided (7 pages). Ordering information is given on any current masthead page.

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[18] One possibility, which is suggested by our recent mechanistic study[5] of iminium ion–alkene cyclizations, would involve rate-determining attack of a nucleophile on a π-complex (or bridged cation) produced from reversible interaction of the iminium ion and alkyne groups.

Simulation of Crystal Structures by Empirical Atom–Atom Potentials. 2. The Orthorhombic-to-Tetragonal Phase Transition in the High-Temperature (T_c > 90 K) Superconductor $YBa_2Cu_3O_{7-y}$

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It is well established from several powder neutron diffraction studies[1] that the Y–Ba–Cu–O phase with the superconducting transition temperature (T_c) greater than 90 K[2] is orthorhombic $YBa_2Cu_3O_{7-y}$ ($y \simeq 0.19$). The important structural unit of this phase is the $Ba_2Cu_3O_{7-y}{}^{3-}$ slab,[1,3] which consists of two CuO_2 layers that sandwich one CuO_3 chain and two Ba^{2+} cations per unit cell (see Figure 1). The copper atoms (Cu2) of the CuO_2 layers are linked to the copper atoms (Cu1) of the CuO_3 chains via the capping oxygen atoms (O4). Band electronic structure studies[3] reveal that the CuO_2 layers of each $Ba_2Cu_3O_{7-y}{}^{3-}$ slab interact via the Cu2–O4–Cu1–O4–Cu2 linkages. Upon increasing temperature in a pure oxygen atmosphere, $YBa_2Cu_3O_{7-y}$ gradually loses the oxygen atoms O1 of the Cu1 atom planes thereby destroying the CuO_3 chains[4a] and eventually undergoes an orthorhombic to tetragonal phase transition near ~1000 K,[4a] which occurs when the stoichiometry of YBa_2O_{7-y} is close to $YBa_2Cu_3O_{6.5}$.[4a]

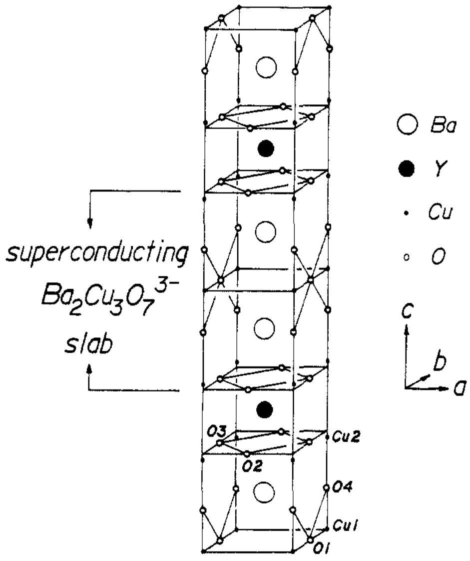

Figure 1. Crystal structure of $YBa_2Cu_3O_{7-y}$ ($y \simeq 0.19$) determined by neutron diffraction.[1a]

Table I. The Atom–Atom Potential Parameters for $Ba^{2+}\cdots Ba^{2+}$ and $Y^{3+}\cdots Y^{3+}$

pair	B (eV)	ρ (Å)	C (eV. Å^6)
$Ba^{2+}\cdots Ba^{2+}$	3749.5	0.350	442.1
$Y^{3+}\cdots Y^{3+}$	6902.5	0.250	18.44

An important structural change in $YBa_2Cu_3O_{7-y}$ induced by increasing the O1 atom vacancies is a Cu1–O4 distance shortening and a Cu2–O4 distance elongation (e.g., Cu1–O4 = 1.850 (3) and 1.800 (6) Å, and Cu2–O4 = 2.303 (3) and 2.486 (10) Å for $YBa_2Cu_3O_{6.81}$[1a] and $YBa_2Cu_3O_{6.42}$,[4a] respectively). Thus an increase in the O1 atom vacancies lenghtens the Cu2–O4–Cu1–O4–Cu2 linkages.

Another structural aspect of importance in $YBa_2Cu_3O_{7-y}$ is the gradual increase in the length of the unit cell *c* parameter with increasing temperature, which is *not* a simple thermal expansion: The *c* parameter, the $Ba^{2+}\cdots Ba^{2+}$ distance, and the $Ba^{2+}\cdots Y^{3+}$ distance are, respectively, 11.6807 (2), 4.306 (7), and 3.688 (3) Å for orthorhombic $YBa_2Cu_3O_{6.81}$ at room temperature,[1a] while they are, respectively, 11.9403 (5), 4.607 (7), and 3.685 (3) Å for tetragonal $YBa_2Cu_3O_{6.42}$ at 1091 K.[4a] The $Ba^{2+}\cdots Y^{3+}$ distance remains nearly constant, so that the increase in the *c* parameter is nearly equal to that in the $Ba^{2+}\cdots Ba^{2+}$ distance.[4a] In fact, with increasing temperature, the Ba^{2+} cations move farther away from the Cu1 atom planes.[4a,5] Even when the room temperature

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[1] (a) Beno, M. A.; Soderholm, L.; Capone, D. W., II; Hinks, D. G.; Jorgensen, J. D.; Schuller, I. K.; Segre, C. U.; Zhang, K.; Grace, J. D. *Appl. Phys. Lett.* **1987**, *51*, 57. (b) Greedan, J. E.; O'Reilly, A.; Stager, C. V. *Phys. Rev. B*: *Condens. Matter* **1987**, *37*, 8770. (c) Capponi, J. J.; Chaillout, C.; Hewart, A. W.; Lejay, P.; Marezio, M.; Nguyen, N.; Raveau, B.; Soubeyroux, J. L.; Tholence, J. L.; Tournier, R. *Europhys. Lett.* **1987**, *3*, 1301. (d) David, W. I. F.; Harrison, W. T. A.; Gunn, J. M. F.; Moze, O.; Soper, A. K.; Day, P.; Jorgensen, J. D.; Beno, M. A.; Capone D. W., II; Hinks, D. G.; Schuller, I. K.; Soderholm, L.; Segre, C. U.; Zhang, K.; Grace, J. D. *Nature* (*London*) **1987**, *327*, 310. (e) Beech, F.; Miraglia, S.; Santoro, A.; Roth, R. S. *Phys. Rev. B*: *Condens. Matter* **1987**, *35*, 8770. (f) Katano, S.; Funahasi, S.; Hatano, T.; Matsushita, A.; Nakamura, K.; Matsumoto, T.; Ogawa, K. *Jpn. J. Appl. Phys., Part 2* **1987**, *26*, L1046. (g) Cox, D. E.; Moodenbaugh, A. R.; Hurst, J. J.; Jones, R. H. *J. Phys. Chem. Solids*, submitted for publication.

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