of the individual rate constants k_1, k_{-1}, and k_2, a composite rate constant $k_{on} = k_1k_2/k_{-1} = K_1k_2$ can be calculated directly (Table I) to describe the formation of the final 2:1 adduct $[\{LCu\}_2(O_2)]^{2+}$ (**3**). This has a negative temperature dependence (i.e., $\Delta H^{\ddagger} = -21$ kJ mol^{-1}), clearly explained by the fact that k_{-1} has a stronger temperature dependence than k_1 and k_2 combined; thus binding of O_2 to form the 2:1 adduct (**3**) is slower at higher temperatures. The overall data analysis leads to the calculated final spectra shown in Figure 1; the spectrum of **3** agrees very closely with that observed under "synthetic" conditions.[2a]

It is interesting to compare the results here with the limited data available in other copper-containing systems[3] as well as for iron and cobalt.[16-18] The present study provides the first full data for 1:1 Cu(I)-dioxygen adduct development, either in protein or synthetic systems. The formation of $[LCu(O_2)]^+$ (**2**) ($k_1 \sim 10^8$ M^{-1} s^{-1}, calcd at 25 °C, Table I) is faster than the rates seen for most LCo(II) 1:1 oxygenation reactions ($k_1 = 10^3$–10^6 M^{-1} s^{-1}, 25 °C).[16] The molecularity of the reaction of O_2 with **1** precludes meaningful comparisons of k_{on} with other Cu_2O_2 complexes derived from discrete dinuclear precursors.[3] However, $k_{on} = 4.4 \times 10^5$ M^{-2} s^{-1} at 25 °C for **3** (6.0×10^7 at −90 °C) parallels ligand-dependent values seen for peroxo–dicobalt(III) (Co_2O_2) complexes analogously derived from mononuclear LCo(II) species.[18] For heme–proteins or porphyrin–Fe^{II} model complexes, the O_2 on-rates ($k_1 \sim 10^6$–10^9 M^{-1} s^{-1}) are similar to that seen for formation of **2**. However, it appears that off-rates for iron species are much smaller, giving rise to larger K_1 values ($K_1 \sim 10^4$–10^6, 20 °C).[16]

For **1** and other nonprotein Cu(I) complexes,[3] the strong low-temperature O_2 binding for either 1:1 or 2:1 adducts is enthalpic in origin.[3] Large negative $\Delta S°$ values preclude room-temperature stability of the Cu_2O_2 synthetic complexes; this effect is not present in the multisubunit protein hemocyanin.[3,19] Co_2O_2 complexes also exhibit large negative $\Delta S°$ values, but considerable room-temperature stabilities ($\log K_{eq} \sim 6$–15)[16,17,18b] are derived from much larger negative $\Delta H°_{formation}$ values (e.g., −120 to −150 kJ/mol).[16,17]

The 1:1 Cu/O_2 species is of considerable interest as the important primary cuprous ion–dioxygen adduct, since its further reduction leads to O_2 activation in both chemical and biological systems.[4-6,20,21] Chemical investigations of Valentine and coworkers[22] and Thompson[23] lead to the formulation of such species as superoxo–cupric complexes (e.g., Cu^{II}–O_2^-), and Thompson was able to isolate a stable solid compound $[LCu(O_2)]$ (L = hydrotris(3,5-dimethyl-1-pyrazolyl)borate, $\nu_{O-O} = 1015$ cm^{-1} for $^{18}O_2$; $\lambda_{max} = 524$ nm ($\epsilon = 600$ M^{-1} cm^{-1}). The structure of this complex was suggested to contain an unsymmetrical terminally coordinated O_2^- ligand, but a symmetric side-on η^2-superoxo ligation probably merits consideration.[24] Further efforts will be aimed at the characterization and reactivity studies of stable analogues of $[LCu(O_2)]^+$ (**2**).

Acknowledgment. We thank the National Institutes of Health (K.D.K.) and Swiss National Science Foundation (A.D.Z.) for support of this research.

Supplementary Material Available: Spectra illustrating the UV–vis changes occurring during the oxygenation of **1** (1 page). Ordering information is given on any current masthead page.

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(16) (a) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137–203. (b) Wilkens, R. G. In *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York, 1988; pp 49–60. (c) Fallab, S.; Mitchell, P. R. *Adv. Inorg. Bioinorg. Mech.* **1984**, *3*, 311–377. (d) Jones, R. D.; Sommerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *2*, 139.

(17) Brouwer, M.; Baker-King, C. *J. Inorg. Biochem.* **1988**, *34*, 117–133.

(18) (a) Bis(L-histidinato)Co^{II}, $k_{on} = 5.5 \times 10^6$ M^{-2} s^{-1} (4 °C): Simplicio, J.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 6092–6095. (b) For Co^{II} complexes of N_4 macrocycles, $k_{on} \sim 10^8$–10^9 M^{-2} s^{-1} (25 °C): Wong, C. L.; Switzer, J. A.; Balakrishnan, K. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5511–5518.

(19) Loss of degrees of freedom of $O_{2(g)}$ provides the major contribution to the negative $\Delta S°$ observed.[3,17]

(20) Roberts, J. L., Jr.; Sawyer, D. T. *Isr. J. Chem.* **1983**, *23*, 430–438.

(21) Superoxide dismutation reactions also involve Cu–O_2 intermediates: Cabelli, D. E.; Bielski, B. H. J.; Holcman, J. *J. Am. Chem. Soc.* **1987**, *109*, 3665–3669, and references cited therein.

(22) Nappa, M.; Valentine, J. S.; Miksztal, A. R.; Schugar, H. G.; Isied, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 7744–7746.

(23) (a) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4057–4059. (b) Thompson, J. S. In *Biological & Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, NY, 1986; Vol. 2, pp 1–10.

(24) For an example of side-on η^2-O_2^- binding in a cobalt complex, see: Egan, J. W., Jr.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445–2446.

Preparation of Functionalized Alkynyl(phenyl)iodonium Salts via a Novel Iodonium-Transfer Process between Alkynylstannanes and PhI^+CN^-OTf

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Alkynyliodonium species, **1**, have become useful reagents for the preparation of monofunctionalized acetylenes and other valuable synthetic transformations.[1-3] However, to date, with the exception of the β-Me_3Si-substituted system (**1**: R = Me_3Si), no β-functionalized alkynyliodonium species are known,[4] the full synthetic potential of these novel tricoordinate iodine species[5] thereby being limited.

$$RC{\equiv}CI^+Ph\,X^-$$

1

Hence in this communication, we report the preparation of a variety of hitherto unknown β-functionalized alkynyl(phenyl)iodonium triflates via a new, unique iodonium-transfer process involving the readily available[6] PhI^+CN^-OTf as the transfer agent.[7]

A variety of functionalized alkynyliodonium salts may be prepared in good yields in a single step by the interaction of the appropriate alkynylstannanes[8] **2** with PhI^+CN^-OTf (Scheme I) in CH_2Cl_2 at low temperature. Compounds **4a–f** are isolated by low-temperature filtration under a N_2 atmosphere and are re-

---

(1) Stang, P. J.; Kitamura, T.; Arif, A. M.; Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **1990**, *112*, 374. Stang, P. J.; Crittell, C. M. *Organometallics* **1990**, *9*, 3191. Stang, P. J.; Kitamura, T.; Boehshar, M.; Wingert, H. *J. Am. Chem. Soc.* **1989**, *111*, 2225. Kitamura, T.; Stang, P. J. *Tetrahedron Lett.* **1988**, *29*, 1887. Stang, P. J.; Boehshar, M.; Wingert, H. *J. Am. Chem. Soc.* **1988**, *110*, 3272. Stang, P. J.; Kitamura, T. *J. Am. Chem. Soc.* **1987**, *109*, 7561. Stang, P. J.; Surber, B. W.; Chen, Z. C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228.

(2) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1990**, *55*, 1513. Margida, A. J.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4707. Carman, C. S.; Koser, G. F. *J. Org. Chem.* **1983**, *48*, 2534.

(3) Ochiai, M.; Ho, T.; Takaoka, M.; Masaki, Y.; Kunishima, M.; Tanis, S.; Nagao, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 118. Ochiai, M.; Kunishima, M.; Nagao, Y.; Fuji, K.; Shiro, M.; Fujita, E. *J. Am. Chem. Soc.* **1986**, *108*, 8281. Ochiai, M.; Kunishima, M.; Suni, K.; Nagao, Y.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *Tetrahedron Lett.* **1985**, 4501.

(4) Stang, P. J.; Arif, A. M.; Crittell, C. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 287. Kitamura, T.; Stang, P. J. *J. Org. Chem.* **1988**, *53*, 4105.

(5) Reviews: Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, *365*. Merkushev, E. B. *Russ. Chem. Rev.* **1987**, *56*, 826. Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. Ochiai, M.; Nagao, Y. *Yuki Gosei Kagaku Kyokaishi* **1986**, *44*, 660. Varvoglis, A. *Synthesis* **1984**, 7099. Koser, G. F. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1983; Suppl. D, Chapters 18 and 25, pp 721–811, 1265–1351. Umenoto, T. *Yuki Gosei Kagaku Kyokaishi* **1983**, *41*, 251. Varvoglis, A. *Chem. Soc. Rev.* **1982**, *10*, 377.

(6) Zhdankin, V. V.; Crittell, C. M.; Stang, P. J.; Zefirov, N. S. *Tetrahedron Lett.* **1990**, 4828.

(7) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1990**, *112*, 6437. Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 4571.

(8) Cauletti, C.; Furlani, C.; Sebald, A. *Gazz. Chim. Ital.* **1988**, *118*, 1. Kleiner, F. G.; Neumann, W. P. *Justus Leibigs Ann. Chem.* **1968**, *716*, 19. Davidsohn, W. E.; Henry, M. C. *Chem. Rev.* **1967**, *67*, 73.

0002-7863/91/1513-5870$02.50/0

Table I. Physical and Spectral Properties of Alkynyliodonium Triflates **4**

compd	% yield	mp dec, °C	IR, cm^{-1}	^{1}H NMR, δ	^{13}C NMR, δ	^{19}F NMR, δ
4a	77	113-114	(Nujol) 3071, 3067, 2158 (C≡C), 1652 (CO), 1598, 1579, 1294, 1241, 1220, 1180, 1162, 1017	($CDCl_3$) 8.15 (d, 2 H), 8.10 (d, 2 H), 7.70 (t, 1 H), 7.63, (t, 1 H), 7.56 (t, 2 H), 7.47 (t, 2 H)	174.9 (CO), 135.5, 135.0, 134.8, 133.1, 132.7, 130.2, 129.1, 119.6 (q, *J* = 319 Hz), 116.7, 101.5 (βC), 40.6 (αC)	-78.3
4b	82	119	(Nujol) 3085, 2153 (C≡C), 1681 (CO), 1562, 1293, 1234, 1217, 1165, 1024	($CDCl_3$) 8.09 (d, 2 H), 7.67 (t, 1 H), 7.53 (t, 2 H), 1.15 (s, 9 H)	190.6 (CO), 134.5, 132.9, 132.5, 119.4 (q, *J* = 318 Hz), 116.7, 101.0 (βC), 45.2, 40.1 (αC), 25.4 (CH_3)	-77.6
4c	72	100-101	(CCl_4) 3061, 2290 (C≡N), 2149 (C≡C), 1562, 1471, 1447, 1263, 1231, 1175, 1017	(CD_3CN) 8.22 (d, 2 H), 7.78 (t, 1 H), 7.62 (t, 2 H)	136.2, 134.5, 133.5, 120.6, (q, *J* = 319 Hz), 117.8, 104.6 (βC), 75.3 (CN), 38.7 (αC)	-78.9
4d	56	117-118	(CCl_4), 3093, 3056, 2987, 2135 (C≡C), 1596, 1471, 1447, 1331 (Ts), 1313, 1265, 1232, 1207, 1161, 1084, 1020	(CD_3CN) 8.11 (d, 2 H), 7.81 (d, 2 H), 7.77 (t, 1 H), 7.58 (t, 2 H), 7.47 (d, 2 H), 2.47 (s, 3 H)	148.7, 137.0, 136.2, 134.6, 133.8, 131.5, 128.8, 118.1, 99.4 (βC), 45.3 (αC), 21.8 (CH_3)	-78.7
4e	42	48-50	(CCl_4) 3056, 2179 (C≡C), 1722 (CO), 1474, 1444, 1334, 1304, 1255, 1231, 1209, 1180, 1023	(CD_3CN) 8.20 (d, 2 H), 7.79 (t, 1 H), 7.62 (t, 2 H), 3.73 (s, 3 H)	*a*	-79.0
4f	77	72-73	(Nujol) 3091, 2190 (C≡C), 1561, 1274, 1243, 1224, 1177, 1166, 1024	($CDCl_3$) 8.05 (d, 2 H), 7.62 (t, 1 H), 7.51 (t, 2 H), 4.35 (s, 2 H), 3.35 (s, 3 H)	134.1, 132.5, 132.3, 119.6 (q, *J* = 318 Hz), 116.4, 104.8 (βC), 60.6 (CH_2), 58.4 (CH_3), 30.2 (αC)	-77.7

[a] Due to the limited solubility and low stability of **4e**, the ^{13}C NMR spectrum was unobtainable.

Scheme I

$$\underset{\mathbf{2}}{YC{\equiv}CSnR_3} + \underset{\mathbf{3}}{PhI^+CN^-OTf} \xrightarrow[-R_3SnCN]{CH_2Cl_2,\ -40\ °C} \underset{\mathbf{4}}{YC{\equiv}CI^+Ph^-OTf}$$

2a: Y = PhC(O), R = Et
b: Y = *t*-BuC(O), R = Et
c: Y = CN, R = Et
d: Y = *p*-$CH_3C_6H_4SO_2$, R = Et
e: Y = $CH_3OC(O)$, R = Et
f: Y = CH_3OCH_2, R = Bu

4a: Y = PhC(O)
b: Y = *t*-BuC(O)
c: Y = CN
d: Y = *p*-$CH_3C_6H_4SO_2$
e: Y = $CH_3OC(O)$
f: Y = CH_3OCH_2

crystallized from CH_2Cl_2/pentane. The pure functionalized iodonium salts, with the exception of **4e**, are stable, white, microcrystalline solids that can be stored at room temperature for several days, whereas salt **4e** turns black at room temperature in a matter of minutes but can be stored at -20 °C for extended periods.

Alkynyliodonium salts **4a-f** were fully characterized[9] by multinuclear NMR and IR as summarized in Table I. Specifically, the infrared spectra display characteristic C≡C signals between 2135 and 2270 cm^{-1} and absorptions due to the triflate as well as the various other functional groups. The ^{1}H NMR spectra display the typical 2:1:2 aromatic resonances between 7.50 and 8.25 ppm characteristic of phenyliodonium species, as well as the appropriate signals for the remaining protons. The ^{13}C NMR spectra are particularly diagnostic of the individual β-functionalized alkynyl(phenyl)iodonium species **4** as summarized in Table I.

Preliminary results indicate that these new functionalized alkynyliodonium salts are highly reactive both toward nucleophiles and in cycloaddition reactions. Hence, we believe that these and related functionalized alkynyl(phenyl)iodonium salts, readily accessible by our newly discovered iodonium-transfer reaction, will greatly extend the already demonstrated synthetic usefulness of these tricoordinate iodine species.

Acknowledgment. Financial support by the National Cancer Institute of the NIH (2ROCA16903) is gratefully appreciated.

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[9] With the exception of **4e**, all new compounds gave satisfactory (±0.4%) C, H, and S analyses.

Absence of Nucleophilic Assistance by Solvent and Azide Ion to the Reaction of Cumyl Derivatives: Mechanism of Nucleophilic Substitution at Tertiary Carbon

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We report the absence of nucleophilic assistance to the reaction of tertiary cumyl derivatives, $XArC(Me)_2Y$, either by azide ion, 1-propanethiol and methanol, or by a solvent of 50:50 (v/v) trifluoroethanol/water.

The role of solvent in the solvolysis of tertiary substrates has attracted wide attention,[1-9] and the importance of nucleophilic

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(1) Doering, W. von E.; Zeiss, H. H. *J. Am. Chem. Soc.* **1953**, *75*, 4733-4738. Swain, C. G.; MacLachlan, A. *J. Am. Chem. Soc.* **1960**, *82*, 6095-6101. Frisone, G. J.; Thornton, E. R. *J. Am. Chem. Soc.* **1968**, *90*, 1211-1215. Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Am. Chem. Soc.* **1984**, *49*, 3639-3641.

(2) Bordwell, F. G.; Wiley, P. F.; Mecca, T. G. *J. Am. Chem. Soc.* **1975**, *97*, 132-136.

(3) (a) Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 2700-2707. (b) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977-5981. (c) Harris, J. M.; Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D. *Tetrahedron Lett.* **1974**, 2331-2334. (d) Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 8147-8156. (e) Shafer, S. G.; Harris, J. M. *J. Org. Chem.* **1981**, *46*, 2164-2169.

(4) (a) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Am. Chem. Soc.* **1979**, *101*, 2486-2488. (b) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244-1252. (c) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741-5747. (d) Bentley, T. W.; Roberts, K. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1055-1060.

(5) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635-4638. Kevill, D. N.; Anderson, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 1579-1585.

(6) Abraham, M. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1343-1357. Abraham, M. H.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1981**, *46*, 3053-3056.

0002-7863/91/1513-5871$02.50/0 © 1991 American Chemical Society