Reaction of μ-Oxobis[(trifluoromethanesulfonato)(phenyl)iodine(III)] with Group 14 Propargyl Derivatives and a Propargyl Ether

Daniel A. Gately, Thomas A. Luther, Jack R. Norton,* Mary M. Miller, and Oren P. Anderson

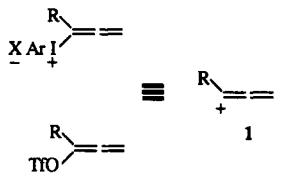
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received June 1, 1992

The treatment of 4,4-dimethyl-1-(trimethylsilyl)-2-pentyne (**4a**) or 4,4-dimethyl-1-(tributylstannyl)-2-pentyne (**4b**) with μ-oxobis[(trifluoromethanesulfonato)(phenyl)iodine(III)] (**2**) gives 4,4-dimethyl-1-(2-iodophenyl)-2-pentyne (**9**). Deuterium labeling has confirmed that propargylation of **2** occurs ortho to the position originally occupied by the I(III). The addition of 2 equiv of **4a** to **2** at −80 °C results in 2 equiv each of **9**, trimethylsilyl triflate (**10**), and *tert*-butylallene (**11**) and 1 equiv of hexamethyldisiloxane (**12**); in contrast, the addition of 2 equiv of **4b** to **2** at −30 °C results in 2 equiv each of **9** and tributylstannyl triflate (**16**). A mechanism that explains these product ratios is proposed. The reaction of **2**-*o*,*o*'-d_2 and **4b** shows the negligible intramolecular kinetic isotope effect (0.99 ± 0.01) expected for what is in effect a Claisen rearrangement. The addition of **2** to 2-butynyl (trimethylsilyl)methyl ether (**20**) affords the single product **21** resulting from anti addition and control of regiochemistry by the ether oxygen. Attempts to desilylate **21** to an allenyl triflate result in the regeneration of the propargyl ether **20**.

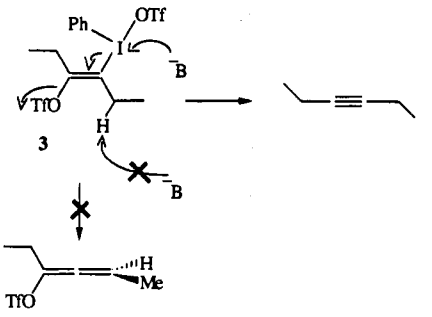
Introduction

Allenes are directly and indirectly involved in substitution and elimination processes, sigmatropic rearrangements, and cycloaddition reactions with allenes, ketenes, olefins, enones, and heterocycles.[1] An allenyl triflate or iodinane would be synthetically equivalent to an sp^2 carbocation **1** in the same way that vinyl triflates[2] and iodinanes[3] are equivalent to sp^2 carbocations and alkynyl esters,[4] iodinanes,[5] and diiodinanes[6] are equivalent to sp carbocations.



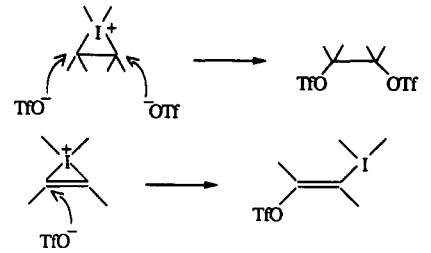
Our first effort to generate an allenyl triflate or iodinane began with the reaction of alkynes with the diaryl di-

Scheme I



(allenyl triflate)

iodinane μ-oxobis[(trifluoromethanesulfonato)(phenyl)-iodine(III)] (**2**) (Zefirov's reagent).[7] The reaction of simple olefins with **2** is known to afford vicinal ditriflates by syn addition,[7a,c,8] presumably by the process in eq 1. With alkynes one would expect the process to stop after anti addition and formation of a vinyliodonium triflate as in eq 2.



(1)

(2)

When we began this work little was known about the reactivity of symmetrical or unsymmetrical[9] alkynes with iodine(III) reagents.[10] We obtained a single product **3**

(1) For a comprehensive review of allenes, see: (a) *The Chemistry of Allenes*; Landor, S. R., Ed.; Academic: London, 1982; Vols. 1–3. (b) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley: New York, 1984.

(2) For reviews of vinyl triflates, see: (a) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85. (b) Stang, P. J.; Rappaport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press, New York, 1979. (c) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107. (d) Subramanian, L. R.; Hanack, M. *J. Chem. Educ.* **1975**, *52*, 80. (e) Stang, P. J. *Prog. Phys. Org. Chem.* **1973**, *10*, 205. (f) Modena, G.; Tonelato, U. *Adv. Phys. Chem.* **1971**, *9*, 185.

(3) For the synthesis and reactivity of vinyl iodinanes, see: (a) Ochiai, M.; Oshima, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7059. (b) Stang, P. J.; Ullmann, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *11*, 1469. (c) Ochiai, M.; Oshima, K.; Masaki, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 869. (d) Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron Lett.* **1988**, *44*, 4095. (e) Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, V. *Tetrahedron Lett.* **1985**, *26*, 2351. (f) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Golstev, A. N. *Dokl. Akad. Nauk. SSSR* **1977**, *235*, 591. (g) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V. *Dokl. Akad. Nauk. SSSR* **1971**, *197*, 1337.

(4) For a recent review of alkynyl esters, see: (a) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *3*, 274. (b) Stang, P. J. *Acc. Chem. Res.* **1991**, *24*, 304.

(5) For the synthesis and reactivity of alkynyl iodinanes, see: (a) Stang, P. J.; Arif, A. M.; Critell, C. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *3*, 287. (b) Kitamura, T.; Stang, P. J. *J. Org. Chem.* **1988**, *53*, 4105. (c) Stang, P. J.; Surber, B. W.; Chen, Z. C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228. (d) Ochiai, M.; Kunishima, M.; Sumi, K.; Nagao, Y.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *Tetrahedron Lett.* **1985**, *26*, 4501. (e) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4700. (f) Koser, G. F.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1981**, *46*, 4324. (g) Also see ref 4a and b.

(6) For the synthesis and reactivity of alkynyl diiodanes, see: (a) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 4571. (b) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1990**, *112*, 6437.

(7) (a) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Y. V.; Koz'min, A. S. *J. Org. Chem. USSR (Engl. Trans.)* **1984**, *20*, 401; *Zh. Org. Khim.* **1984**, *20*, 446. (b) Gallos, J.; Varvoglis, A.; Alcock, N. W. *J. Chem. Soc., Perkin Trans. 1* **1985**, 757. (c) Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Org. Chem.* **1987**, *52*, 3650.

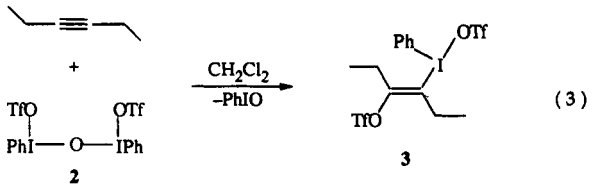
(8) (a) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Y. V.; Sovokin, V. D.; Semerikov, V. N.; Koz'min, A. S.; Caple, R.; Berglund, B. A. *Tetrahedron Lett.* **1986**, *27*, 3971. (b) Zefirov, N. S.; Koz'min, A. S. *Acc. Chem. Res.* **1985**, *18*, 154.

(9) Stang and co-workers recently established the regioselective anti addition of PhIOH(OTf) **17** to terminal acetylenes, see: Kitamura, T.; Taniguchi, H.; Stang, P. J.; *Tetrahedron Lett.* **1990**, *31*, 703.

(10) In the interest of clarity, the schemes and eqs in this paper show the iodine(III) atom covalently bound to the triflate oxygen (I–OTf). However, such bonds are more ionic (I^+OTf^-) than covalent (see ref 5a, 6, and the X-ray structure of **21** in this work), and the triflates may be fully dissociated under some conditions.

0022-3263/92/1957-6496$03.00/0

(which we assumed to possess an *E* configuration[9]) from the reaction of 3-hexyne with **2** (eq 3).

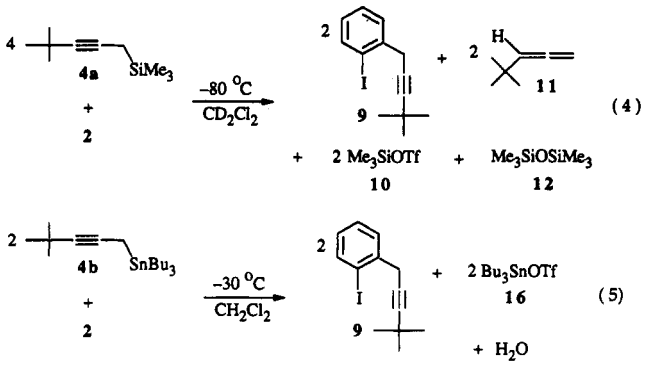


(3)

We then treated **3** with a variety of bases in an effort to deprotonate the carbon β to the iodonio leaving group and form an allenyl triflate. The result, however, was largely the regeneration of 3-hexyne (Scheme I).

We then treated the propargylsilane **4a** and the propargylstannane **4b** with **2**. We expected that the iodonium-bridged intermediate **5** would be most stable as the carbocation **6** stabilized by β silicon or tin,[11] and we thus expected the product of the reaction of **4** and **2** to be **7** as depicted in Scheme II. (We hoped to desilylate or destannylate **7** to the allenyliodinane **8**.)

To our surprise the result, shown in eqs 4 and 5, was the formation of the rearranged propargyliodoarene **9**.



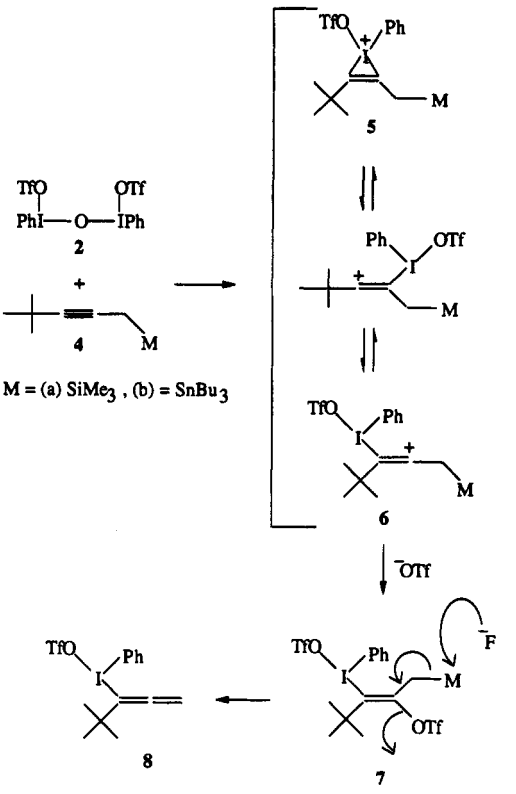
(4)

(5)

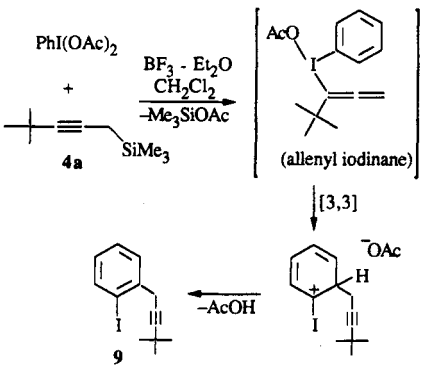
While we were investigating the mechanism of the formation of **9** and the reasons why **4a** and **4b** reacted differently with **2**, Ochiai and co-workers published their observation that propargyliodoarenes were generated from the reaction of monoaryl iodinanes with propargylsilanes, -germanes, or -stannanes.[12] They proposed that desilylation of an iodonium cation intermediate led to an allenyl iodinane and that an iodonio Claisen rearrangement of the latter led to **9** (Scheme III).[12] Although they were unable to isolate the allenyliodinane, they did (i) find that the propargyliodoarenes were formed intramolecularly,[12] (ii) determine the regioselectivity of the orthopropargylation of some ring-substituted monoaryl iodinanes,[12] and (iii) isolate meta-substituted propargyl iodoarenes (and in some cases ipso-substituted propargyl arenes) when both ortho positions of the monoaryl iodinane substrate were occupied by alkyl substituents.[12,13]

In this paper we explore the differences between the reaction of the propargylsilane **4a** with **2** (eq 4) and that of the propargylstannane **4b** (eq 5). We also report a deuterium labeling result that establishes the site of propargylation of **2** in the absence of substituents and the intramolecular kinetic isotope effect for the ortho-

Scheme II



Scheme III



propargylation of **2**-*o*,*o*'-d_2 with **4b**. Finally, we report the regiospecific anti addition of **2** to a propargyl ether, as well as the results of attempts to convert the resulting vinyliodonium triflate into an allenyl triflate.

Results and Discussion

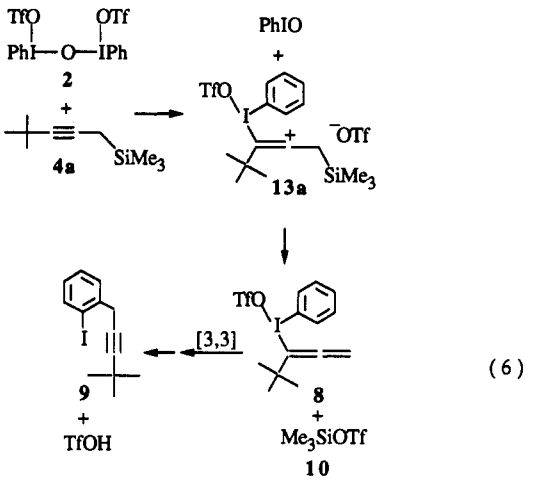
Reaction of 4a with Zefirov's Reagent, 2. The addition of the propargylsilane **4a** to **2** resulted in a dark green-brown solution at -80 °C in CD_2Cl_2. A careful survey of the reaction mixture by ^1H and ^{13}C NMR revealed the presence of the propargyliodoarene **9**, trimethylsilyl triflate (**10**), *tert*-butylallene (**11**), hexamethyldisiloxane (**12**), and iodobenzene. The ratios of products **9**–**12** were determined by ^1H NMR at -80 °C and are consistent with those predicted by the stoichiometry in eq 4 within ±5%.

The first steps of a mechanism that accounts for the stoichiometry in eq 4 are shown as eq 6. Electrophilic addition of 1 equiv of **2** consumes the *first* equiv of **4a**, leading, after loss of iodosylbenzene (PhIO), to the formation of the silyl vinyl cation **13a**.[12] Cleavage of the trimethylsilyl group from **13a** by triflate ion results in the allenyl iodinane **8**[12,13] and Me_3SiOTf (**10**). The [3,3] sigmatropic rearrangement of **8** results in the *first* equiv of

(11) For examples of the β effect of Si, Ge, and Sn: (a) Ullrich, H.; Kaufmann, F. P.; Apeloig, Y.; Braude, V.; Danovich, D.; Berndt, A.; Stamatis, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *11*, 1479. (b) Nguyen, K. A.; Gordon, M. S.; Wang, G.; Lambert, J. B. *Organometallics* **1991**, *10*, 2798. (c) Dallaire, C.; Brook, M. A. *Organometallics* **1990**, *9*, 2873.

(12) Ochiai, M.; Ito, T.; Takaoka, Y.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1319.

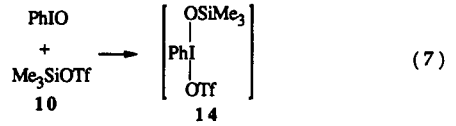
(13) Ochiai, M.; Ito, T.; Masaki, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 15.



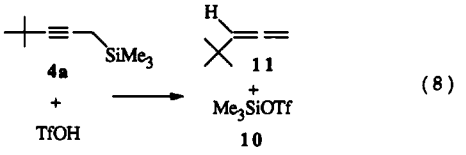
(6)

the propargyliodoarene **9** and 1 equiv of triflic acid (TfOH).[12,13]

O-silylation of the iodosylbenzene from eq 6 by the **10** also formed therein affords the monoaryliodinane **14** (eq 7). The triflic acid from eq 6 desilylates the *second* equiv



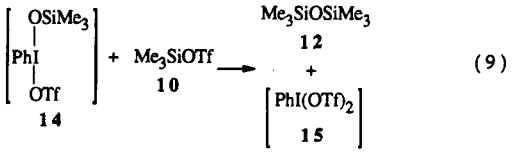
(7)



(8)

of **4a** to give the *first* equiv of *tert*-butylallene, **11**, and to regenerate **10** (eq 8). (The formation of terminal allenes like **11** by the desilylation of propargylsilanes with acids is common;[14] the formation of **10** and **11** from **4a** and 1 equiv of TfOH at −80 °C in CD_2Cl_2 can be observed by ^1H NMR.)

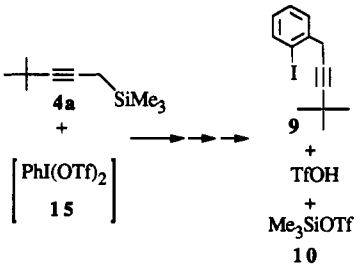
Another equiv of **10** combines with **14** and gives the monoaryliodonium ditriflate **15** and 1 equiv of hexamethyldisiloxane, **12** (eq 9). (Equations 7 and 9 find



(9)

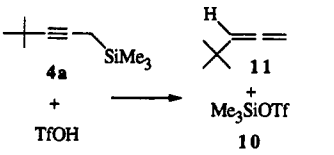
precedent in the known formation of the monoaryliodinane **15** and the hexamethyldisiloxane **12** from 2 equiv of **10** and iodosylbenzene.[15])

The monoaryliodonium ditriflate **15** adds to the *third* equiv of **4a** and produces the *second* equiv of **9**, another equiv of **10**, and triflic acid (eq 10).



(10)

The triflic acid formed in eq 10 desilyates the *fourth* equiv of **4a** to give the *second* equiv of **11** and the *second* equiv of **10** (eq 11).

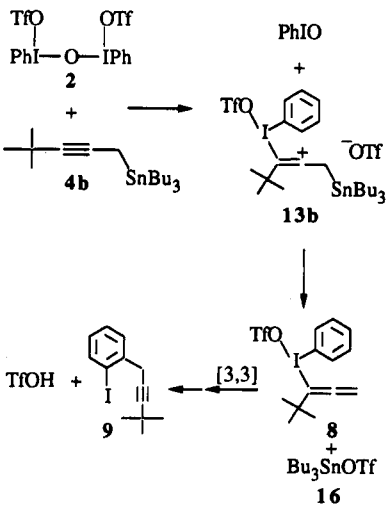


(11)

The combined operation of eqs 6–11 produces the stoichiometry in eq 4.

Reaction of 4b with Zefirov's Reagent, 2. The propargylstannane **4b** reacted cleanly with **2** at −30 °C in CH_2Cl_2 (or in $CHCl_3$). The principal products were the propargyliodoarene **9** and tributylstannyl triflate (**16**),[16] in yields consistent with the stoichiometry in eq 5 (84% GC yield of **9** if **4b**:**2** = 2:1, 41% GC yield of **9** if **4b**:**2** = 1:1). A small amount of *tert*-butylallene (**11**) (4–8%) was also observed.

The first steps of a mechanism that accounts for the stoichiometry in eq 5 are shown as eq 12. Electrophilic



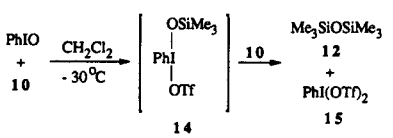
(12)

addition of 1 equiv of **2** consumes the *first* equiv of **4b**, leading, after loss of iodosylbenzene (PhIO), to the formation of the stannyl vinyl cation **13b**.[12] Cleavage of the tributylstannyl group from **13b** by triflate ion results in the same allenyliodinane **8** formed in eq 6 and in Bu_3SnOTf (**16**). The [3,3] sigmatropic rearrangement of **8** results again in the *first* equiv of the propargyliodoarene **9** and 1 equiv of triflic acid (TfOH).

Some of the triflic acid from eq 12 destannylates **4b** to give *tert*-butylallene (**11**) and to regenerate **16** (eq 13).

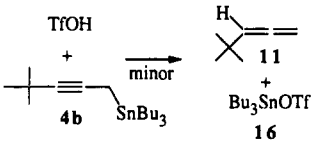
However, most of the iodosylbenzene formed in eq 12 reacts with the triflic acid also formed therein to afford the monoaryl iodinane **17** (eq 14).

(14) Flood, T.; Peterson, P. *J. Org. Chem.* **1980**, *45*, 5006.
(15) At −30 °C in CH_2Cl_2

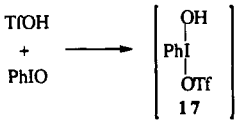


(a) Zefirov, N. S.; Safronov, S. O.; Kaznacheev, A. A.; Zhdankin, V. V. *J. Org. Chem. USSR (Engl. Trans.)* **1990**, *20*, 1633; *Zh. Org. Khim.* **1990**, *20*, 1807. (b) Zhdankin, V. V.; Critell, C. M.; Stang, P. J.; Zefirov, N. S. *Tetrahedron Lett.* **1990**, *34*, 4821.

(16) ^1H and ^{13}C NMR data of **16** were obtained from an authentic sample prepared by a known procedure: Xian, Y. T.; Fouf, P.; Guibe, F.; Balavoine, G. *Nouv. J. Chem.* **1984**, *10*, 611.

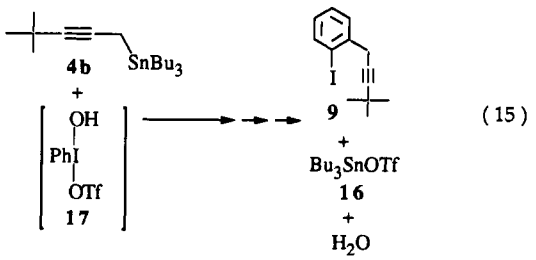


(13)



(14)

The addition of the monoaryl iodinane **17** to the *second* equiv of **4b** results in the *second* equiv each of **9** and **16** plus 1 equiv of water (eq 15).[17]



(15)

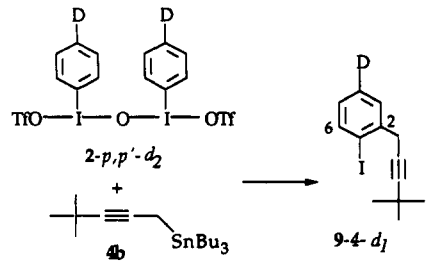
The combined operation of eqs 12, 14, and 15 produces the stoichiometry of the major products shown in eq 5. The presence of **11** as a minor product at the end of the reaction reflects the occasional operation of eq 13.

Comparison of the Reactions of 4a vs 4b with 2. The propargyl iodoarene **9** appears to be formed in the same fashion, i.e., by the [3,3] sigmatropic rearrangement of the allenyliodinane intermediate **8**, whether the propargylsilane **4a** or the propargylstannane **4b** is the starting material. (Compare eq 6 with eq 12). The difference between the 4:1 **4a/2** stoichiometry in eq 4 and the 2:1 **4b/2** stoichiometry in eq 5 must arise from a difference between the *subsequent* chemistry of the PhIO, Me_3SiOTf (**10**), and TfOH formed in eq 6 and the *subsequent* chemistry of the PhIO, Bu_3SnOTf (**16**), and TfOH formed in eq 12.

An explanation for this difference is suggested by the report that the Sn in **16** is "much less acidic towards oxygen atoms" than the Si in **10**.[16] Thus, the silylation of PhIO by **10** (eq 7) is probably much faster than its Sn analogue, the reaction of PhIO with **16**. More PhIO may thus remain in the tin case to react with TfOH (eq 14) and eventually with additional propargyl reagent (eq 15). This explanation does require a significant delay between the formation of PhIO and **10** or **16** and the release of TfOH, implying the accumulation of the allenyliodinane intermediate **8**.

Positional Selectivity of the Propargylation of an Unsubstituted Phenyl Iodinane. In order to test the hypothesis that the formation of **9** from **8** occurred by the [3,3] sigmatropic rearrangement depicted in eqs 6 and 12, we determined the site of propargylation of **2**-*p,p'*-d_2. (The latter was prepared by oxidizing *p*-deuterioiodobenzene[18] and treating the resulting *p*-deuterioiodosylbenzene with Tf_2O.[7c]) The treatment of **2**-*p,p'*-d_2 with **4b** resulted in **9** with no ^1H resonance at δ 7.36 ppm (H4) and a singlet at δ 7.61 ppm (H3), which was thus **9**-*4*-d_1 (eq 16)—the result expected from the [3,3] sigmatropic rearrangement in eqs 6 and 12.

Intramolecular Deuterium Kinetic Isotope Effect. In an effort to elucidate the detailed mechanism of orthopropargylation we determined the intramolecular H/D



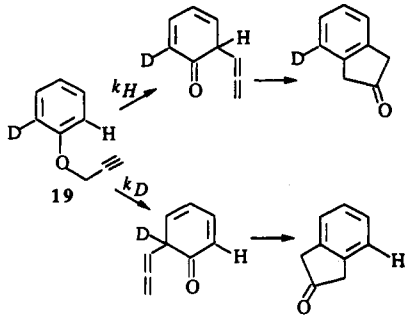
(16)

isotope effect associated with the reaction. The required starting material, **2**-*o,o'*-d_2, was prepared by oxidizing *o*-deuterioiodobenzene[19] and treating the resulting *o*-deuterioiodosylbenzene with Tf_2O.[7c]) The treatment of **2**-*o,o'*-d_2 with **4b** gave a product ratio (**9**/**9**-*6*-d_1 in Scheme IV) of 0.99 ± 0.01 as determined by mass spectrometry.

The absence of an intramolecular isotope effect has implications for the mechanism of formation of **9** from **8**. The rate-determining step in the latter process (we assume the rate-determining step in the overall reaction to be the formation of **8**) cannot be the deprotonation in the last step of Scheme IV (which should display a sizable primary isotope effect). The **8** → **9** rate-determining step must therefore be the k_H/k_D one in Scheme IV.

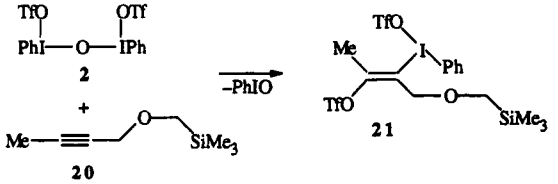
The secondary isotope effect associated with that k_H/k_D step must be very small, despite the fact that it results in rehybridization from the sp^2 C–H(D) in **8**-*o*-d_1 to the sp^3 C–H(D) in **18**. The situation is like that in electrophilic aromatic substitutions when the formation of the σ complex is rate-determining;[20] such reactions also show negligible isotope effects despite the fact that they result in rehybridization from sp^2 to sp^3.

A negligible intramolecular isotope effect has also been observed for a propargyl-to-allenyl Claisen rearrangement. Al-Sader and Al-Fekri[21] have reported a k_H/k_D value of 1.00 ± 0.01 for the 2-deuteriophenyl propargyl ether (**19**, eq 17).



(17)

Regiospecific Anti Addition of Zefirov's Reagent, 2, to the Propargyl Ether 20. When 1 equiv of **2** was added to a solution of the propargyl ether **20**, only a single product (**21**) was formed (eq 18).



(18)

The regio- and stereochemistry of **21** have been determined by X-ray crystallography. The results (Figure 1)

(17) After several days at room temperature, a saturated solution of water in CD_2Cl_2 did not react with **16**.

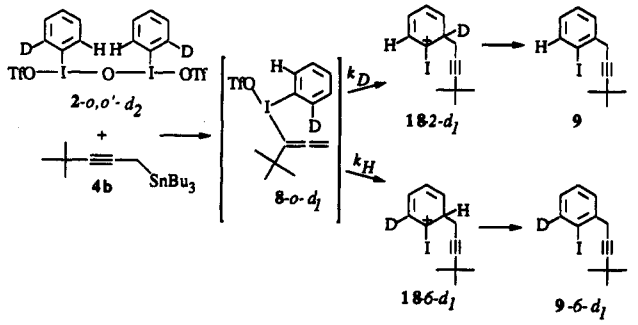
(18) Kasai, P. H.; Hedaya, E.; Whipple, E. B. *J. Am. Chem. Soc.* **1969**, *91*, 4364.

(19) Edmundson, R. S.; Wrigley, J. O. L. *Tetrahedron* **1967**, *23*, 283.

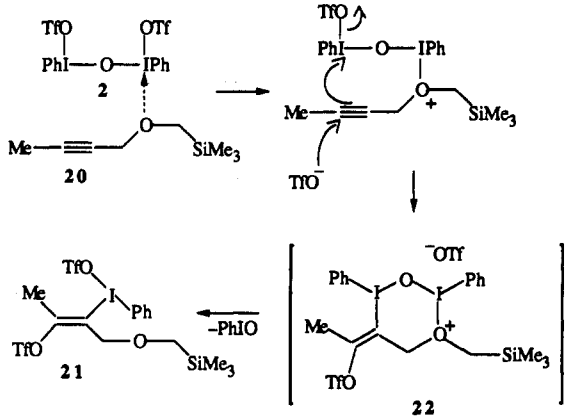
(20) (a) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 162–167. (b) McMichael, K. D.; Korver, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 2746. (c) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum: New York, 1990; pp 543–544.

(21) Al-Sader, B. H.; Al-Fekri, D. M. *J. Org. Chem.* **1978**, *43*, 3627.

Scheme IV



Scheme V



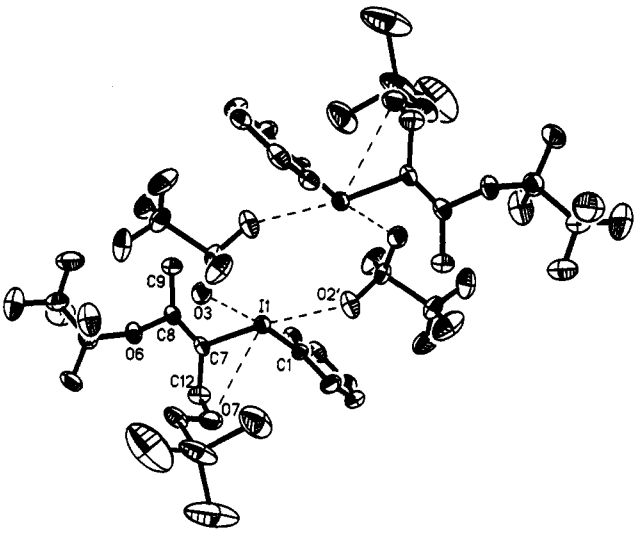


Figure 1. Structure of the dimer of the vinyliodonium triflate **21**. Thermal ellipsoids have been drawn at the 50% probability level.

confirm that it has the structure shown in eq 18, with the (*E*) configuration about the double bond expected from the mechanism in eq 2.

The ether oxygen in **20** apparently controls the regiochemistry with which it reacts with **2**. After the ether oxygen of **20** coordinates to the first iodine(III) of **2**, the second iodine(III) of **2** presumably adds to the triple bond of **20** (Scheme V) to give the iodinane intermediate **22** containing a six-membered ring. The bright yellow color of the homogeneous solution that results immediately after **20** is added to **2** is characteristic of a bridging I–O–I group;[22] the white precipitate of iodosylbenzene does not

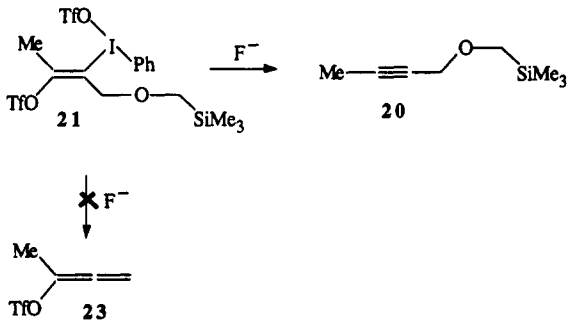
(22) Dasent, W. E.; Waddington, T. C. *J. Chem. Soc.* **1960**, 3350.

Table I. Significant Distances (Å) and Angles (deg)[a] for the Vinyliodonium Triflate 21

Bond Distances			
I1–C1	2.103 (7)	C7–C8	1.335 (12)
I1–C7	2.110 (6)	C7–C12	1.498 (12)
I1–O3	2.819 (6)	C8–C9	1.475 (12)
I1–O2′	2.864 (5)	O6–C8	1.451 (8)
I1–O7	3.213 (5)	O7–C12	1.404 (11)
Bond Angles			
C1–I1–C7	92.7 (3)	I1–C7–C12	113.5 (5)
C1–I1–O3	173.9 (2)	O6–C8–C7	113.7 (6)
C7–I1–O2′	173.7 (3)	O6–C8–C9	112.8 (6)
O7–I1–C7	48.5 (2)	O7–C12–C7	112.1 (6)
I1–O7–C12	70.0 (4)	C7–C8–C9	133.4 (6)
I1–C7–C8	117.4 (5)	C8–C7–C12	129.1 (6)

[a] Numbers in parentheses are esd values.

Scheme VI



appear for some time, suggesting the accumulation of either the **2**/**20** adduct or **22**.

Molecular Structure of 21. As Figure 1 shows, **21** crystallizes as a centrosymmetric dimer. Selected bond distances and angles for **21** are given in Table I. If we consider only one monomeric unit (C1, C7, and O3 around I1) the iodine(III) coordination geometry is T-shaped, as expected for a 10-I-3 system.[23] Within the T the C1(Ph)–I1–C7 (vinyl) angle is 92.7(3)° and the C1(Ph)–I1–O3 (triflate) angle is 173.9(2)°. However, secondary bonding[24a] to the triflate of the other monomer (O2′) makes the actual iodine(III) coordination geometry planar (the I1–O2′ distance is only 0.045 Å longer than the I1–O3 distance, and the C7–I1–O2′ angle is 173.7(3)°). The situation is analogous to that reported by Drück and Littke for an iodonium ylide with two carbonyl oxygens coordinated to the I(III); in the ylide structure a secondary bonded oxygen is only slightly further (3.138 Å) from the I(III) than the oxygen completing the T (2.965 Å).[24b]

The ether oxygen O7 responsible for the regiospecificity with which **21** is formed lies 3.213 (5) Å from I1. Although this distance exceeds that of reported secondary bonds, it may reflect a weak bonding interaction; the sum of the van der Waals radii of O and I is 3.5.[25]

Attempted Desilylation of 21. Several attempts (anhydrous KF/crown ether,[26] $KF{\cdot}2H_2O/Bu_4NCl$,[27] and Bu_4NF in THF) to desilylate[28] **21** to an allenyl triflate (**23**)

(23) Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.
(24) (a) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1. (b) Drück, U.; Littke, W. *Acta Crystallogr.* **1978**, *B34*, 3092.
(25) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper: New York, 1983; pp 258–259.
(26) Murray, T. F.; Norton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4107.
(27) Carpino, L. A.; Sau, A. C. *J. Chem. Soc., Chem. Commun.* **1979**, 514.
(28) A similar desilylation involving the loss of ethylene rather than formaldehyde is known; see: Seiber, P. *Helv. Chim. Acta* **1977**, *Fasc. 8*, Nr 264.

failed (Scheme VI). As in Scheme I, the fluoride ion attacks the iodine(III)[29] center in **21** to regenerate **20**.

Experimental Section

Materials. All air-sensitive compounds were prepared and handled under a nitrogen atmosphere using standard bench-top techniques and Schlenk glassware.[30] Tetrahydrofuran and diethyl ether were distilled under N_2 from sodium benzophenone ketyl. Dichloromethane and hexane were dried and distilled from CaH_2. Chloroform and dichloromethane-d_2 were dried over CaH_2 for >48 h, degassed by freezing at −196 °C, evacuating, and thawing three times, and finally transferred into a flame-dried vacuum bulb. 4,4-Dimethyl-1-(trimethylsilyl)-2-pentyne (**4a**),[31] iodosylbenzene,[32] and **2**[7c] were prepared by standard procedures.

Low-Temperature Reaction of 4a with Zefirov's Reagent (2). The propargylsilane **4a** (55 μL, 0.277 mmol) was added by syringe to a 5-mm NMR tube containing **2** (100 mg, 0.139 mmol) and CD_2Cl_2 by vacuum transfer (~0.7 mL) at −90 °C (EtOH/liquid N_2 slush bath). The solution was degassed, thawed at −90 °C, and sealed. The NMR tube containing the heterogeneous mixture was introduced into an NMR probe precooled to −90 °C and allowed to warm to −80 °C. The NMR revealed iodobenzene, hexamethyldisiloxane (**12**; ^{1}H NMR: δ 0.01 (s). ^{13}C NMR: δ −0.24), Me_3SiOTf (**10**; ^{1}H NMR: δ 0.44 (s). ^{13}C NMR: δ 1.25), 4,4-dimethyl-1-(2-iodophenyl)-2-pentyne[12] (**9**; ^{1}H NMR: δ 7.77 (d), 7.66 (d), 7.35 (m, overlaps with the proton in the para position of iodobenzene), 6.95 (t), 3.49 (s), 1.21 (s)), and *tert*-butylallene (**11**; ^{1}H NMR[33a]: δ 5.08 (dd, J = 6.6 Hz), 4.69 (d, J = 6.6 Hz), 0.97 (s). ^{13}C NMR[33b]: δ 204.8, 97.7, 72.1). The presence of **10** and **12** was confirmed by the addition of authentic samples to the product mixture at room temperature.

4,4-Dimethyl-1-(tributylstannyl)-2-pentyne (4b). In our hands, the reported method for the preparation of **4b**[34] afforded substantial amounts of Bu_4Sn as well as the desired product; a modified preparation of **4b** follows. *n*-Butyllithium (6.9 mL, 17.3 mmol, 2.5 M) was added over 10 min to a solution of 4,4-dimethyl-2-pentyne (3 mL, 22.4 mmol) and THF (15 mL) while the temperature was maintained at −7 °C. After being stirred for 15 minutes, the solution was warmed to room temperature and stirred for 1 h. The resulting solution was cooled to −7 °C, treated with Bu_3SnCl (3.6 mL, 13.25 mmol), and warmed to room temperature. After 30 min, the solution was poured into 50 mL of saturated NH_4Cl–50 mL of ether, and the aqueous phase was extracted with ether (3 × 50 mL); the combined extracts were washed with brine and then dried over $MgSO_4$. The solvents were removed and the residue spotted on a Chromatotron plate and eluted with pentane. Bu_4Sn (R_f 0.47) and **4b** (R_f 0.27) were separated. Compound **4b** was Kugelrohr distilled (bp 87–93 °C (0.02 Torr)) to yield 3.32 g (65%). ^{1}H NMR ($CDCl_3$): δ 1.50 (m, 6 H), 1.48 (s, 2 H), 1.31 (m, 6 H), 1.16 (s, 9 H), 0.90 (m, 15 H). ^{13}C NMR ($CDCl_3$): δ 86.7, 78.4, 31.7, 29.0 ($^3J_{CSn}$ = 10.21 Hz), 27.7, 27.3 ($^2J_{CSn}$ = 26.51 Hz), 13.6, 9.8 ($^1J_{CSn}$ = 253.52 Hz), −4.1. IR (neat): 2219 cm^{-1} (C≡C). Anal. Calcd for $C_{19}H_{38}Sn$: C, 59.24; H, 9.94. Found: C, 59.25; H, 9.94.

Preparation of 4,4-Dimethyl-1-(2-iodophenyl)-2-pentyne (9)[12] from the Treatment of 2 with 4b. A suspension of **2** (804 mg, 1.11 mmol) in $CHCl_3$ (10.0 mL) was prepared in a flame-dried 25-mL Schlenk flask under N_2. The suspension was cooled to −30 °C (EtOH/liquid N_2 slush bath) and treated with **4b** (857 mg, 830 μL, 2.22 mmol). The GC yield of **9** was 558 mg (84%). ^{1}H and ^{13}C NMR spectra of the reaction mixture revealed the presence of **11** (4–8%).[33] The IR spectrum showed 1955 cm^{-1} for the C=C=C asymmetric stretch.[33a] The ^{1}H and ^{13}C NMR of the same mixture agreed with that of the authentic sample of Bu_3SnOTf (**16**) described below.[16] The ^{1}H NMR revealed 54% of **9** to 46% of **16**. The $CHCl_3$ was removed in vacuo and hexane (20 mL) added to the residue. The upper layer was removed with a 2-mL glass pipette; the lower layer was extracted with hexane (3 × 15 mL), and the combined extracts were washed with brine and then dried over $MgSO_4$. The hexane was removed, and the residue was Kugelrohr distilled (0.02 Torr, bp 90–95 °C) to yield 357 mg (54%) of **9** with >95% purity (as determined by ^{1}H NMR). The comparison of ^{1}H NMR chemical shifts of iodobenzene[35] with the chemical shifts and multiplicities in the phenyl region of **9** were used to assign the ^{1}H NMR chemical shifts of the protons at positions 3–6 of **9**; the doublets must correspond to H3 and H6, and the former can be distinguished by the fact that it collapses to a singlet when H4 is replaced by deuterium (see below). ^{1}H NMR ($CDCl_3$): δ 7.83 (H6, d, 1 H), 7.64 (H3, d, 1 H), 7.36 (H4, t, 1 H), 6.94 (H5, t, 1 H). ^{13}C NMR ($CDCl_3$): δ 140.3, 139.1, 128.9, 128.3, 128.1, 99.8, 92.7, 75.4, 31.5, 31.3, 27.6. IR (neat): $\nu_{C=C}$ 2204 cm^{-1}.

Tributylstannyl triflate (16) was prepared as described.[16] ^{1}H NMR ($CDCl_3$): δ 1.63 (m, 6 H), 1.36 (m, 12 H), 0.90 (t, J = 7.27 Hz, 9 H). ^{13}C NMR ($CDCl_3$): δ 27.3 ($^3J_{CSn}$ = 13.22 Hz), 26.7 ($^2J_{CSn}$ = 37.22 Hz), 21.3 ($^1J_{CSn}$ = 183.8 Hz), 13.3. ^{19}F NMR ($CDCl_3$): δ −78.1.

2-*p*,*p*'-d_2 was prepared as described[7c] from *p*-deuterioiodosylbenzene. The latter was made by the procedure[32] standard for its isotopically normal analogue from p-deuterio(diacetoxy)-iodobenzene, itself prepared by the procedure[36] standard for its isotopically normal analogue from *p*-deuterioiodobenzene[18] (^{1}H NMR ($CDCl_3$): δ 7.45 (d, 2 H), 7.09 (d, 2 H). ^{13}C NMR ($CDCl_3$): δ 137.5, 130.1, 127.1 (t, J = 25 Hz), 94.3. IR (neat): ν_{C-D} 2252 cm^{-1}) and *p*-deuteriobromobenzene[18] (^{1}H NMR ($CDCl_3$): δ 7.39 (d, 2 H), 7.12 (d, 2 H). ^{13}C NMR ($CDCl_3$): δ 131.5, 129.9, 126.6 (t, J = 24 Hz), 122.5. IR (neat): ν_{C-D} 2255 cm^{-1}. ^{1}H NMR of the *p*-deuteriobromobenzene showed >99% deuterium incorporation).

9-4-d_1. The procedure for this reaction was similar to that described above for the treatment of **2** with **4b** with the exception that $CHCl_3$ was replaced with CH_2Cl_2 and **2** was replaced with **2-*p*,*p*'-d_2**. The ^{1}H NMR of the isolated **9-4-d_1** (recall that the GC yield of **9** in this reaction, determined above is 84%) revealed (>99%) a 1:1:1 ratio of a *doublet* (H6)—the proton ortho to the iodine in **9**, a *singlet* (H3)—the proton ortho to the propargyl moiety of **9**, and a *doublet* (H5)—the proton para to the propargyl moiety in **9**; the assignments of the ring protons of **9** have been discussed above in connection with its preparation. ^{1}H NMR ($CDCl_3$): δ 7.80 (H6, d, 1 H), 7.61 (H3, s, 1 H), 6.92 (H5, d, 1 H), 3.58 (s, 2 H), 1.28 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 140.4, 139.2, 128.9, 128.1, 128.4 to 127.7 (apparent t overlapped with δ 128.1, J = 49 Hz), 99.8, 31.5, 31.3, 27.6.

2-*o*,*o*'-d_2 was prepared from *o*-deuterioiodobenzene by the method described above for the generation of **2-*p*,*p*'-d_2**. The required precursor *o*-deuteriochlorobenzene[37] was prepared by quenching the *o*-lithiochlorobenzene anion with a 2-fold excess of CH_3OD. The spectra of *o*-deuteriochlorobenzene not previously reported were as follows. ^{1}H NMR ($CDCl_3$): δ 7.40–7.24 (m). ^{13}C NMR ($CDCl_3$): δ 134.3, 129.6, 129.5, 128.6, 128.3, 126.3 (apparent t overlapped with δ 128.3, J = 25 Hz). Its ^{1}H NMR showed >99% deuterium incorporation. *o*-Deuterioiodobenzene was prepared from *o*-deuteriochlorobenzene by a reported procedure[19] with the following modifications. Magnesium metal (1.39 g, 56.2 mmol) in THF (25 mL) was treated with *o*-deuteriochlorobenzene (5.99 g, 52.7 mmol) and was refluxed for 36 h. To the Grignard reagent was added a saturated I_2/anhydrous ether solution (70 mL, 66.2 mmol) at −7 °C over a 45-min period. The workup procedure was similar to that described for the isolation of *p*-deuterioiodobenzene.[18] For *o*-deuterioiodobenzene. ^{1}H NMR ($CDCl_3$): δ 7.69 (d, 1 H), 7.29 (t, 1 H), 7.12–7.06 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 137.4, 137.0 (apparent t overlapped with δ 137.4, J = 25 Hz), 130.1, 129.9, 127.3, 94.2.

(29) When fluoride ion was added to (*E*)-β-alkylvinyliodonium tetrafluoroborates, Ochiai and co-workers observed the selective attack on the alkylidene proton rather than the iodine(III) center; see ref 3a.

(30) Shriver, D. F. *The Manipulation of Air Sensitive Compounds*; McGraw-Hill: New York, 1969.

(31) Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry 1*; Springer-Verlag: New York, 1987; p 64.

(32) Saltzman, H.; Sharefkin, J. G. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 658.

(33) (a) Lilje, K. C.; Macomber, R. S. *J. Org. Chem.* **1974**, *24*, 3600. (b) Janssen, R. H. A. M.; Lousberg, R. J. J. Ch.; deBie, M. J. A. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 85.

(34) Rajagopalan, S.; Zweifel, G. *Synthesis* **1984**, 111.

(35) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*; Wiley: New York, 1981; p 231.

(36) Sharefkin, J. G.; Saltzman, H. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 660.

(37) See ref 31, p 213.

Intramolecular Kinetic Isotope Effect. 2-*o,o'*-d_2 + 4b. This reaction was carried out by the procedure described above for 9-*4*-d_1 with the exception that 2-*p,p'*-d_2 was replaced with 2-*o,o'*-d_2. The intensities of the *m/e* 298–300 peaks of the 9/9-*6*-d_1 mixture were used to determine the value of 9/9-*6*-d_1 by an overdetermined least-squares procedure (program MassSpec): (EI, 70eV) *m/z* (intensity) 298 (632), M; 299 (732), M + 1; 300 (91), M + 2. For 9/9-*6*-d_1. ^{1}H NMR ($CDCl_3$): δ 7.79 (H6, d, 1 H), 7.62 (H3, d, 2 H), 7.35 (H4, t, 2 H), 6.92 (H5, m, 2 H), 3.58 (s, 4 H), 1.28 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 140.1, 139.1, 138.4 (apparent overlapped with δ 139.1, *J* = 25 Hz), 128.9, 128.3, 128.1, 128.0, 99.8, 99.7, 92.7, 75.3, 31.5, 31.3, 27.5.

2-Butynyl (Trimethylsilyl)methyl Ether (20). To a well-stirred mixture of NaH powder (3.37 g, 140.4 mmol) in anhydrous ether (50 mL) was added 2-butyn-1-ol (6.56 g, 93.6 mmol) over a 1-h period; the mixture was then allowed to stir for an additional 3 h. To this gray slurry was added Me_3SiCH_2OTf[38] (18 mL, 90.0 mmol) in anhydrous ether (50 mL) over a 45-min period and the stirring continued for an additional 24 h. The solution was cautiously added to a 1:1 ether/CH_3OH solution until the exothermicity of the reaction ceased. The layers were separated, the aqueous phase was extracted with ether (3 × 75 mL), and the combined extracts were washed with brine and then dried over $MgSO_4$. The ether was removed by evaporation and the residual oil distilled (bp 50 °C (10 Torr)); isolated yield, 11.7 g (80%). ^{1}H NMR ($CDCl_3$): δ 4.02 (q, *J* = 1.9 Hz, 2 H), 3.13 (t, *J* = 1.4 Hz, 2 H), 1.83 (t, *J* = 1.8 Hz, 3 H), 0.02 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 81.5, 75.7, 63.5, 62.3, 3.1, −3.3. The ^{1}H NMR revealed >95% purity.

Preparation of the Vinyliodonium Triflate 21. A suspension of **2** (1117 mg, 1.55 mmol) in CH_2Cl_2 (30 mL) was prepared in a flame-dried 100-mL Schlenk flask under N_2. To the lemon-yellow suspension was added **20** (266 mg, 1.70 mmol) whereupon the solution turned homogeneous lemon-yellow. After 48 h the mixture became cloudy as a white precipitate formed. The solvent was concentrated to 5 mL. A layer of anhydrous hexane (15 mL) was added. The resulting off-white precipitate was isolated by filtration (632 mg, 63%) and dried under vacuum (0.001 Torr) overnight. Crystals suitable for X-ray structure determination were grown out of a 10:1 ethyl acetate/hexane mixture; the crystals obtained (clear, colorless needles) were dried overnight and then mounted on the diffractometer under a stream of N_2. ^{1}H NMR (CD_2Cl_2): δ 8.15 (d, 2 H), 7.73 (t, 1 H), 7.54 (t, 2 H), 4.28 (s, 2 H), 3.29 (s, 2 H), 2.66 (s, 3 H), 0.09 (s, 9 H). ^{13}C NMR (CD_2Cl_2): δ 155.0, 135.7, 133.4, 132.8, 121.2, 112.7, 71.2, 66.9, 23.2, −3.0. ^{19}F NMR (CD_2Cl_2): δ −73.8, −78.7. Anal. Calcd for $C_{16}H_{21}F_6IO_7S_2Si$: C, 29.19; H, 3.21; F, 17.31; I, 19.28; S, 9.74; Si, 4.27. Found: C, 29.01; H, 3.12; F, 17.28; I, 19.45; S, 9.70; Si, 4.10.

X-ray Analysis of 21. $C_{16}H_{21}F_6IO_7S_2Si$, M_r = 658.4; monoclinic, *C2/c*, *a* = 29.431 (14) Å, *b* = 8.364 (2) Å, *c* = 22.328 (5) Å, β = 108.24 (2)°, *V* = 5220 (3) Å^3, *Z* = 8, D_x = 1.68 g cm^{-3}; λ (Mo Kα) = 0.7107 Å, μ = 1.51 mm^{-1}, *F*(000) = 2608, *T* = 143 K, *R* = 0.056 (*wR* = 0.063) for 3562 unique, observed reflections.

Crystal size 0.12 × 0.12 × 0.50 mm. Siemens P4 diffractometer, unit cell constants from least-squares fit of setting angles for 25 reflections ($2\theta_{av}$ = 20.76°). Data collected (ω scans) to (sin θ)/λ = 0.5947 Å^{-1}, $-36 \le h \le 0$, $-10 \le k \le 0$, $-27 \le l \le 27$. Three standard reflections (200, 020, 002) every 97; Lorentz and polarization corrections; semiempirical absorption correction applied, maximum transmission = 0.720, minimum transmission = 0.689;[39] 4584 unique reflections, 3562 reflections with $F_o > 2.5\sigma(F_o)$ observed.

Structure solved by direct methods. Full-matrix (298 parameters total, data/parameters = 12.0) weighted [$w = (\sigma^2(F) + gF^2)^{-1}$, $g = 1.3 \times 10^{-4}$] least-squares refinement on *F*. H atoms in idealized positions (C–H = 0.96 Å, $U(H) = 1.2 \times U_{iso}(C)$). Non-H atoms refined with anisotropic thermal parameters. At convergence ($(\Delta/\sigma)_{max}$ = 0.012, $(\Delta/\sigma)_{mean}$ = 0.002 for last 3 cycles) *R* = 0.056, *wR* = 0.063, *S* = 1.11, $(\Delta\rho)_{max}$ = 1.4 e Å^{-3} (near I1 (0.75 Å)), $(\Delta\rho)_{min}$ = −0.62 e Å^{-3}. Neutral atom scattering factors and anomalous dispersion corrections were used;[40] all calculations were performed using the SHELXTL program library.[39]

Attempts to Desilylate 21.[28] A suspension of 18-crown-6 (240 mg, 0.911 mmol) and anhydrous KF (240 mg, 4.13 mmol) in $CDCl_3$ (3 mL) was prepared in a flame-dried 15-mL Schlenk flask under N_2. To the suspension was added **21** (204 mg, 0.310 mmol), and the white slurry was stirred for 18 h. The volatile components were vacuum transferred (0.001 Torr) into a flame-dried 15-mL Schlenk flask. The only products identifiable by ^{1}H and ^{13}C NMR were iodobenzene and the propargyl ether **20**. IR analysis of the nonvolatile and volatile components showed no evidence for an allene (no asymmetric C=C=C stretch in the 2000–1900 cm^{-1} region).

Similar results were obtained when $KF \cdot 2H_2O$ (94 mg, 1.00 mmol) and Bu_4NCl (1139 mg, 4.1 mmol)[27] in CD_3CN (5 mL) were treated with **21** (724 mg, 1.10 mmol). No evidence for an allene was seen in the IR when Bu_4NF (TBAF) (720 μL, 0.720 mmol, 1.0 M) was stirred with a solution of **21** (233 mg, 0.354 mmol) in THF (2.5 mL) for a month.

Acknowledgment. We acknowledge Don Dick and David K. Morita for collecting the mass spectrum of 9/9-*6*-d_1 and helping with the GC analyses. We also thank Jonathan Filley, Christophe Lawrie, and David Collum (Cornell) for helpful discussions. This work was funded by Department of Energy Grant DE-FG02-84ER13299-A008.

Supplementary Material Available: Tables of X-ray crystal and structural data for **21** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(38) The alternative reagent Me_3SiCH_2I affords the undesired alkyl and silyl ethers; see: Chakraborty, T. K.; Reddy, G. V. *J. Chem. Soc., Chem. Commun.* **1989**, 251.

(39) Sheldrick, G. M. SHELXTL, Unix Ver. 4.2; Siemens Analytical X-Ray Instruments, Inc.; Madison, WI, 1991.

(40) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

A Novel Synthesis of 2-Aminochromones via Phosgeniminium Salts

Joel Morris,* Donn G. Wishka, and Yue Fang

Medicinal Chemistry Research, The Upjohn Company, Kalamazoo, Michigan 49001

Received June 25, 1992

A novel method for the synthesis of antiplatelet 2-aminochromones making use of the reaction of 2′-hydroxyacetophenone–BF_2 complexes with phosgeniminium chlorides has been developed. Aqueous hydrolysis of the intermediate β-chlorovinylogous amide–BF_2 complex affords the 2-aminochromone in good yield, without the need for chromatographic purification.

Interest in the 2-aminochromone class of compounds relates to its novel antiplatelet activity.[1,2] Research in this area may lead to novel agents useful for the treatment of unstable angina or as adjuncts to conventional thrombo-

0022-3263/92/1957-6502$03.00/0