range effects and the difference in temperature and solvent are taken into account.[16-18] These peaks are not likely due to impurities, satellites, or spinning side bands since they are not present in the room-temperature spectrum run under identical conditions. From the Lorentzian heights of corresponding peaks for the two conformers, the amount of axial present at −90 °C was calculated to be 0.45–0.50%, in excellent agreement with previous results.[19] The small temperature effects observed for equatorial methylcyclohexane between −70 and −90 °C are also in

agreement with results for similar systems.[17]

The excellent agreement between these directly observed shifts for the axial conformer and those predicted from spectral data for dimethylcyclohexanes[16] firmly establishes the use of ^{13}C NMR for the study of conformational behavior of cyclic systems.

(16) Vierhapper, F. W.; Willer, R. L. *Org. Magn. Reson.* **1977**, *9*, 13.
(17) Schneider, H.-J.; Freitag, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 478.
(18) van de Ven, L. J. M.; de Haan, J. W. *J. Phys. Chem.* **1982**, *86*, 2516, and references cited therein. Especially: Tiffon, B.; Doucet, J.-P. *Can. J. Chem.* **1976**, *54*, 2045.
(19) Subbotin, O. A.; Sergeyev, N. M.; Chlopkov, V. N.; Nikishova, N. G.; Bundel', Y. G. *Org. Magn. Reson.* **1980**, *13*, 259.

# Acetylenic Esters. Preparation and Mechanism of Formation of Alkynyl Tosylates and Mesylates via Tricoordinate Iodonium Species

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Contribution No. 4207 from the Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112, and Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware 19898. Received August 15, 1986

Abstract: The preparation and characterization of the first acetylenic esters of any kind (alkynyl tosylates, RC≡COTs, and mesylates, RC≡COMs) is reported. A simple, two-step procedure, starting from commercially available iodosobenzene diacetate, was employed in the synthesis. The final step involved ligand–ligand coupling in a tricoordinate iodonium species, $C_6H_5I(OTs)C≡CR$, via metal complexing. X-ray data indicate an ionic structure for the precursor alkynylphenyliodonium tosylate, $C_6H_5I^+C≡CC_6H_5\cdot^-OTs$. A metal assisted nucleophilic acetylenic displacement, via an addition–elimination process, is suggested as the most likely mechanism for this novel main group ligand–ligand coupling reaction.

Esters of all types, carboxylate **1**, sulfonate **2**, and phosphate **3**, are ubiquitous and play a key role in organic as well as biochemistry.[1] Likewise, their unsaturated counterparts, enol esters **4–6**, are well-known, important, and widely used in synthetic as

Scheme I
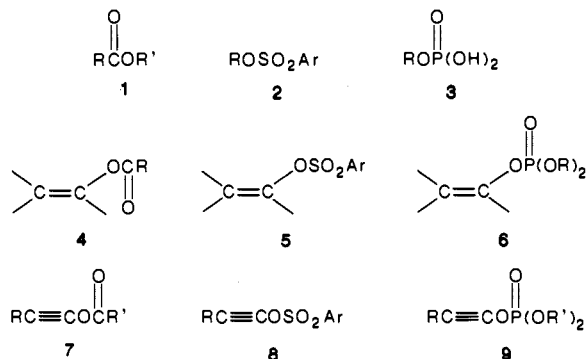
well as mechanistic organic chemistry and biochemistry. Surprisingly, despite the importance and wide uses of esters, simple acetylenic esters of any kind, carboxylate **7**, sulfonate **8**, or phosphate **9**, are, to our knowledge, unknown. This is all the more
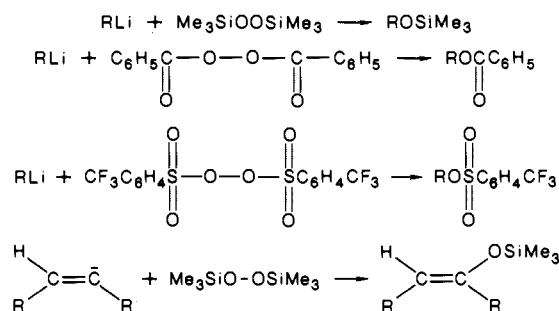
puzzling, since a wide variety of functionalized acetylenes **10** with diverse substituents are well-known and generally stable.[2]
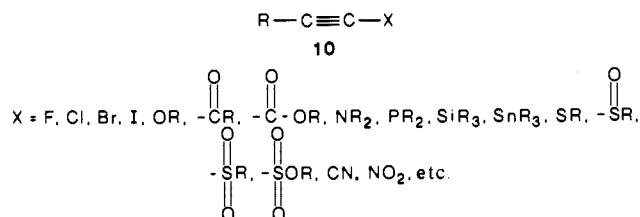
[†] The University of Utah.
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Alkynyl Tosylates and Mesylates

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Scheme II

Scheme III

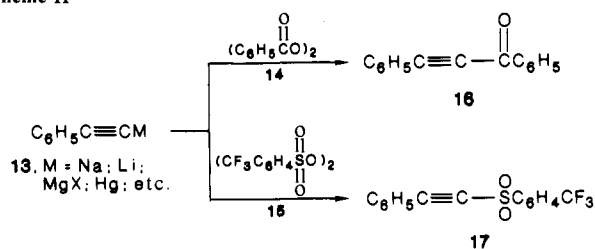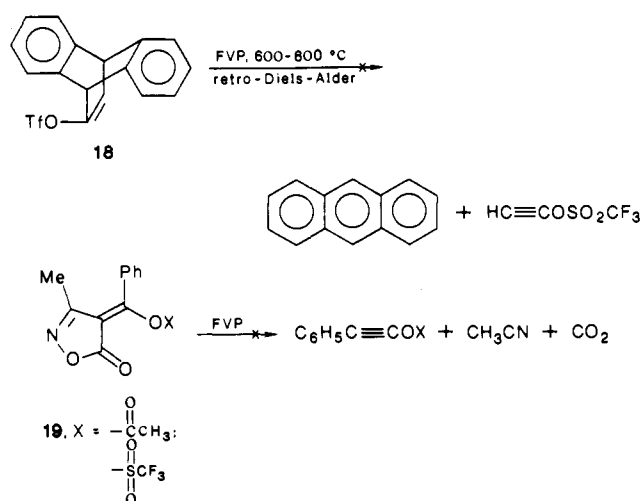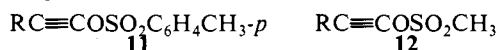Hence, we wish to report the preparation by a simple, general procedure of a variety of alkynyl tosylates 11 and mesylates 12, the first representatives of the family of acetylenic esters 7–9.

$$RC\equiv COSO_2C_6H_4CH_3\text{-}p \qquad RC\equiv COSO_2CH_3$$
$$\mathbf{11} \qquad\qquad\qquad \mathbf{12}$$

Results and Discussions

Acetylenes, including functionalized ones, are generally prepared[2] by one of three common procedures: (a) elimination methods, (b) nucleophilic substitutions, and (c) pyrolysis and/or rearrangement techniques. In our experience none of these obvious methods worked for the preparation of any of the unknown acetylenic esters 7–9. Specifically, elimination methods, mostly dehydrohalogenations of appropriate olefin precursors, gave either no reaction under mild conditions or tar under forcing conditions.[3] Likewise, in spite of the well-known reaction[4] of alkyl and vinyl anions with a variety of peroxides (Scheme I) to give the respective esters or silyl ethers, the analogous reaction of a variety of acetylide anions 13 with either benzoyl peroxide, 14, or sulfonylperoxide 15, gave only the corresponding ketone 16 and sulfone 17, respectively, in greater than 80% isolated yields[5] (Scheme II).

Similarly, flash vacuum pyrolysis (FVP)[6] of either enol triflate 18 or isoxazoles 19 failed to give the desired acetylenic esters,[5] as seen in Scheme III.

(1) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 2nd ed.; McGraw-Hill: New York, 1977. House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981. Walsh, C. *Enzymatic Reaction Mechanisms*; W. H. Freeman: San Francisco, 1979.

(2) For reviews and pertinent references, see: Patai, S. *The Chemistry of Carbon–Carbon Triple Bond*; Wiley-Interscience: London, 1978; Parts I and 2. Jäger, V.; Viehe, H. G. In *Methoden der Organischen Chemie (Houben-Weyl)*; Georg Thieme Verlag: Stuttgard, Germany, 1977; Chapter I, pp 1–916. Viehe, H. G. *Chemistry of Acetylenes*; Marcel Dekker: New York, 1969.

(3) Treptow, W. G. Ph.D. Dissertation, The University of Utah, Salt Lake City, UT, 1979.

(4) See, for example: Brandes, D.; Blaschette, A. *J. Organomet. Chem.* **1974**, *73*, 217–227. Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785–2812. Hoffman, R. V., private communication.

(5) Stang, P. J.; Maas, G.; Ladika, M., unpublished results.

(6) Brown, R. F. C. *Pyrolitic Methods in Organic Chemistry*; Academic Press: New York, 1980.

Scheme IV
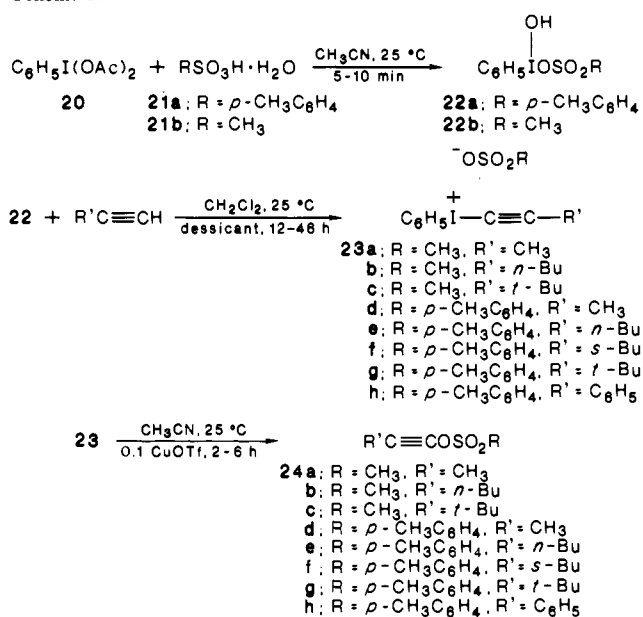
Our successful preparation[7] of these previously unknown, novel alkynyl sulfonates, involving tricoordinate iodonium intermediates, is outlined in Scheme IV.

Reaction of iodosobenzene diacetate,[8] 20, with the monohydrate of sulfonic acid 21, according to Koser and co-workers[9] affords the stable, crystalline iodonium salts 22 (vide infra) in excellent yields. Treatment of 22 with a variety of terminal alkynes by procedures analogous to those of Koser et al.[10] gives alkynylphenyl iodonium sulfonates 23 in reasonable yields as isolable crystalline solids. Although no direct experimental evidence exists yet, it is reasonable to assume that this step occurs via the initial electrophilic addition of the iodonium salt 22 to the alkyne to give either a vinyl cation 25 or a bridged iodonium ion 26 as the first intermediate.[11]
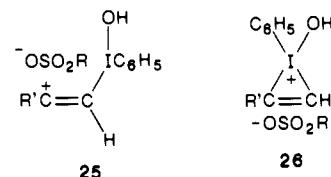
Stirring of iodonium sulfonates 23 in acetonitrile with catalytic amounts (0.05–0.1 equiv) of a variety of metal systems [CuOTf, AgOTf, AgOTs, $(Ph_3P)_4Pd$] affords the desired alkynyl sulfonate esters 24 in good isolated yields along with 1 equiv of iodobenzene. The metal catalyst, preferably CuOTf[12] or AgOTf, is essential for clean reactions under mild conditions. With the exception of 24h, all other pure alkynyl sulfonates (both mesylates and tosylates) are *stable*, pale yellow, viscous oils. The phenylethynyl tosylate 24h is reasonably stable in solution but decomposes in a matter of hours when neat.

Characterization of Alkynyl Sulfonates. Structural assignments of these new alkynyl esters rests upon spectral and chemical data. Specifically, as detailed in the Experimental Section, chemical

(7) For a preliminary report, see: Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452.

(8) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, pp 508–509. Also available from Aldrich.

(9) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476. See, also Neiland, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 889.

(10) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4700. Koser, G. F.; Rebrovic, L.; Wettach, R. H. *Ibid.* **1981**, *46*, 4324.

(11) For a review on such electrophilic additions to alkynes to give vinyl cations, see: Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979.

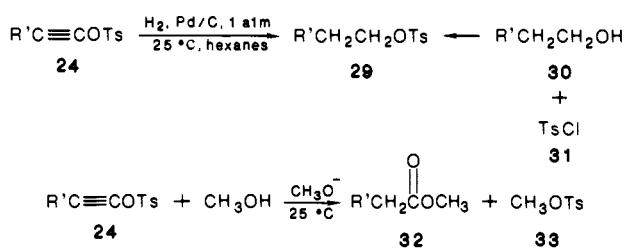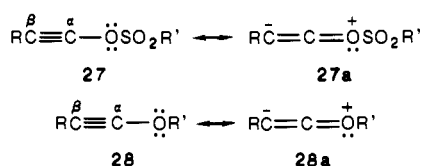(12) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843.

Scheme V

$$R'C{\equiv}COTs \xrightarrow[\text{25 °C, hexanes}]{\text{H}_2,\ \text{Pd/C, 1 atm}} R'CH_2CH_2OTs \longleftarrow R'CH_2CH_2OH$$
$$\textbf{24} \qquad\qquad \textbf{29} \qquad\qquad \textbf{30}$$
$$+$$
$$TsCl$$
$$\textbf{31}$$

$$R'C{\equiv}COTs + CH_3OH \xrightarrow[\text{25 °C}]{CH_3O^-} R'CH_2\overset{\displaystyle O}{\overset{\|}{C}}OCH_3 + CH_3OTs$$
$$\textbf{24} \qquad\qquad\qquad\qquad \textbf{32} \qquad \textbf{33}$$

Table I. Crystal Data

formula	$C_{21}H_{17}O_3SI$
fw	476.33
a, Å	16.039 (4)
b, Å	8.564 (2)
c, Å	15.162 (4)
β, deg	107.14 (2)
space group	$p2_1/n$
Z	4
D_{calcd}, g cm^{-3}	1.59
μ (Mo Kα), cm^{-1}	16.78

ionization mass spectra, by using methane as the ionizing gas, affords in all instances appropriate molecular ions, ion clusters, and fragmentation patterns. In the infrared there are very characteristic *intense* absorptions centered around 2270 cm^{-1} due to the unsymmetrical carbon–carbon triple bond and three strong absorptions centered around 1395 and 1185 cm^{-1} characteristic for the antisymmetric and symmetric SO$_2$ vibrations of sulfonates and at 685 cm^{-1} for the C–O–S absorption of the tosylate. The proton NMR spectra are consistent with the proposed structures, including the typical and familiar aromatic tosylate pattern and the mesylate CH$_3$ absorption at around 3.0 ppm.

Particularly characteristic and valuable are the ^{13}C NMR and especially the signals due to the acetylenic carbons. In all instances the α C's are in the normal acetylenic region of 70–90 ppm. In contrast the β C's are uniformly shifted upfield by about 30 ppm. Sulfonates, despite their electron-withdrawing nature by induction, are known[13] to be electron donating by resonance. Therefore, the acetylenic group in these alkynyl sulfonates is in fact electron rich. This upfield shift of the β C's is due to the contribution of the resonance hybrid **27a** in analogy to alkoxyalkynes **28** where the β C for EtC≡COEt is at 36 ppm and the α C is in the normal position of 74 ppm.[14]

$$\overset{\beta}{R}\overset{\alpha}{C}{\equiv}\overset{..}{\underset{..}{C}}-\overset{..}{\underset{..}{O}}SO_2R' \longleftrightarrow R\overset{-}{C}{=}C{=}\overset{+}{O}SO_2R'$$
$$\textbf{27} \qquad\qquad\qquad \textbf{27a}$$

$$\overset{\beta}{R}\overset{\alpha}{C}{\equiv}\overset{..}{\underset{..}{C}}-\overset{..}{\underset{..}{O}}R' \longleftrightarrow R\overset{-}{C}{=}C{=}\overset{+}{O}R'$$
$$\textbf{28} \qquad\qquad \textbf{28a}$$

Chemical proof for the structure of alkynyl sulfonates **24** comes from hydrogenation and methanolysis studies as shown in Scheme V.

Hydrogenation of **24** affords saturated tosylate **29** identical in all respects with authentic samples prepared by standard procedures from the appropriate alcohols **30** and tosyl chloride. Similarly, basic methanolysis gives saturated esters **32** via RC≡C—O$^-$ or the ketenes RCH=C=O along with the expected methyl tosylate **33** identical in all respects with known authentic products. Hence, the identity of these new alkynyl sulfonates is firmly established.

X-ray Structure Determination of Phenylethynyl Phenyliodonium Tosylate, 23h. In order to assist in both the structure determination and the mechanism of formation of these alkynyl sulfonates as well as to establish the exact molecular structure of a tric-

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(14) Levy, G. C.; Lighter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980; pp. 90–95.

Table II. Final Coordinates ($\times 10^4$) of Non-Hydrogen Atoms for $C_{21}H_{17}O_3SI^a$

atom	x/a	y/b	z/c
I	1729.4 (11)	845.8 (18)	639.8 (12)
S	−366 (4)	2157 (8)	892 (5)
O1	566 (11)	2473 (20)	1060 (14)
O2	−558 (14)	910 (21)	1427 (14)
O3	−784 (15)	1995 (21)	−95 (14)
C1	−751 (16)	3916 (28)	1254 (16)
C2	−1584 (16)	3865 (29)	1366 (16)
C3	−1906 (20)	5202 (32)	1652 (18)
C4	−1484 (20)	6637 (34)	1699 (20)
C5	−688 (17)	6683 (31)	1520 (18)
C6	−349 (15)	5306 (24)	1257 (15)
C7	−1930 (20)	8135 (31)	1885 (20)
C8	2759 (18)	−219 (30)	470 (18)
C9	3390 (19)	−813 (35)	372 (19)
C10	4197 (21)	−1549 (33)	267 (21)
C11	4261 (22)	−1796 (34)	−613 (23)
C12	5082 (22)	−2527 (39)	−647 (25)
C13	5623 (26)	−3186 (43)	69 (26)
C14	5541 (28)	−2871 (43)	924 (29)
C15	4785 (22)	−2131 (36)	1040 (24)
C16	2409 (15)	2911 (24)	1201 (15)
C17	3203 (18)	2706 (36)	1923 (19)
C18	3634 (19)	4067 (35)	2277 (19)
C19	3342 (21)	5454 (39)	1926 (21)
C20	2599 (19)	5660 (35)	1238 (19)
C21	2098 (16)	4271 (30)	824 (16)

^{a} Esd's are in parentheses.

Table III. Selected Bond Lengths (Å) and Nonbonded Contacts for $C_{21}H_{17}O_3SI$

(A) Nonbonded Contacts with Iodine	
I$\cdots$O1	2.556 (19)

(B) Bond Lengths for $C_{21}H_{17}O_3SI$	
I–C8	1.969 (30)
I–C16	2.120 (21)
S–O1	1.465 (18)
S–O2	1.429 (22)
S–O3	1.455 (21)
S–C1	1.776 (26)
C8–C9	1.181 (44)
C9–C10	1.490 (47)

(C) Ranges and Average for Ring Systems^a

ring	range	average
C1–C6	1.377–1.405	1.385 (9)
C10–C15	1.301–1.425	1.386 (26)
C16–C21	1.328–1.469	1.379 (26)

^{a} Error estimates are of the form $\alpha(dc - c) = \sum(d_i - \bar{d_i})^2/(\eta(\eta - 1))^{1/2}$.

**Table IV.** Selected Bond Angles (deg) For $C_{21}H_{17}O_3SI$

(A) Involving Iodine	
C8–I–C16	95.0 (10)
O1$\cdots$I–C8	170.9 (8)
O1$\cdots$I–C16	76.8 (8)
S–O1–I	129.7 (10)

(B) Around Sulfur	
O1–S–O2	114.8 (12)
O1–S–O3	109.5 (14)
O2–S–O3	113.7 (12)
C1–S–O1	102.7 (11)
C1–S–O2	107.8 (13)
C1–S–O3	107.6 (11)

Table V. Selected Dihedral Angles for $C_{21}H_{17}O_3SI$

C8–I–O1–S	20.8 (53)
C16–I–O1–S	4.8 (16)
I–C16–C17–C18	0.0 (28)
I–C16–C21–C20	−0.3 (21)
C16–I–C8–C9	−165.3 (65)

Table VI. Hydrogen Coordinates for $C_{21}H_{17}O_3SI^a$

atom	x/a	y/b	z/c
H2	−0.1928 (16)	0.2943 (29)	0.1243 (16)
H3	−0.2442 (20)	0.5162 (32)	0.1799 (18)
H5	−0.0383 (17)	0.7640 (31)	0.1540 (18)
H6	0.0175 (15)	0.5343 (24)	0.1085 (15)
H7A	−0.1570 (20)	0.9028 (31)	0.1923 (20)
H7B	−0.2073 (20)	0.8018 (31)	0.2447 (20)
H7C	−0.2450 (20)	0.8262 (31)	0.1390 (20)
H11	0.3801 (22)	−0.1524 (34)	−0.1147 (23)
H12	0.5182 (22)	−0.2524 (39)	−0.1234 (25)
H13	0.6092 (26)	−0.3807 (43)	0.0005 (26)
H14	0.5992 (28)	−0.3220 (43)	0.1447 (29)
H15	0.4742 (22)	−0.2024 (36)	0.1649 (24)
H17	0.3423 (18)	0.1706 (36)	0.2149 (19)
H18	0.4145 (19)	0.4006 (35)	0.2788 (19)
H19	0.3665 (21)	0.6364 (39)	0.2174 (21)
H20	0.2410 (19)	0.6670 (35)	0.1003 (19)
H21	0.1574 (16)	0.4343 (30)	0.0328 (16)

^{a} Esd's are in parentheses.

Figure 2. Ψ-TBP geometry of the 10-I-3 species **23h** and **22a**.

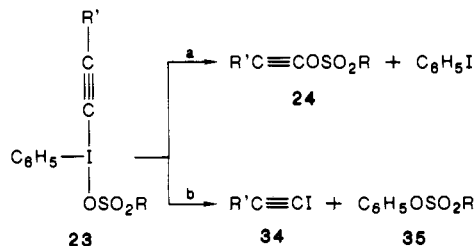**Scheme VI**
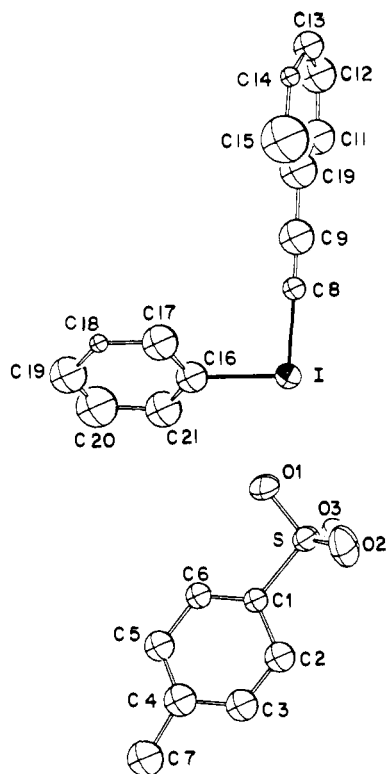
Figure 1. ORTEP drawing of **23h**.

oordinate alkynyl iodonium species an X-ray determination was carried out on tosylate **23h**. A colorless platelet shaped crystal of **23h** was examined by standard X-ray procedures. The relevant crystal and structural data are summarized in Tables I–VI and on the ORTEP structure shown in Figure 1.

The data reveal that **23h** is a 10-I-3 species in the J. C. Martin formalism[15] with a distorted pseudotrigonal bipyramidal geometry (Ψ-TBP) as indicated in Figure 2. Closer examination of the data reveals a number of salient features about **23h**. In particular, the I–O bond length of 2.56 Å is unusually long and well outside the computed covalent single bond length of 1.99 Å. This fact, coupled with the near identity of all three S–O bond lengths at 1.43–1.45 Å, strongly suggests an ionic character for this compound. Similar results and conclusions were obtained by Koser et al.[16] based on the X-ray of the analogous **22a** also shown in Figure 2. Specifically, in this phenyl hydroxyiodonium tosylate two distinct I–O distances were observed at 1.94 Å for the covalent

I–OH and 2.47 Å for the ionic I–OTs with near equal S–O bonds also at 1.43–1.47 Å. Moreover, X-ray data are available for a number of tricoordinate iodine species such as $C_6H_5I(OAc)_2$,[17] $C_6H_5ICl_2$,[18] and others,[19,20] all indicating a Ψ-TBP geometry or T-shaped molecule (ignoring the I lone pairs) and possible ionic character.

Mechanism of Formation of Alkynyl Sulfonates 24 from the Tricoordinate Iodonium Species 23. In a formalistic sense the formation of esters **24** from **23** represents a ligand–ligand coupling in a tricoordinate main group species analogous to the well-precedented ligand–ligand coupling in organometallic chemistry by reductive eliminations.[21] As indicated in Scheme VI there are two modes of ligand–ligand couplings possible for **23**. Path a couples the alkyne with the sulfonate and the iodine with the phenyl group resulting in the desired alkynyl sulfonates **24** and iodobenzene. Path b with reverse couplings gives undesired iodoalkynes **34** and phenyl sulfonates **35**. A priori it is difficult to predict which pathway should predominate. However, we know that metal catalysis is essential for the clean formation of esters **24**. In the absence of metal catalysis no reaction occurs at room temperature. At higher temperatures ("thermolyses" in refluxing benzene) or photochemical decomposition, the reaction yields a preponderance of iodoalkynes and phenyl sulfonates (path b) and only minor amounts (if any) of the alkynyl esters **24**.

At least three reasonable mechanisms may be envisioned for this novel ligand–ligand coupling process, as outlined in Scheme VII. Path A involves single electron transfer (SET) and radical intermediates. Such a pathway is well precedented in diazonium salt[22] and peroxide[23] decompositions catalyzed by copper(I) ions. Moreover, iodonium salts are known to have reduction potentials comparable to diazonium ions.[24]

Path B involves copper(III) intermediates analogous to the species recently proposed by Lockhart[25] for the Cu(I)-catalyzed

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(16) Koser, G. F.; Wettach, R. H.; Troup, J. M.; Frenz, B. A. *J. Org. Chem.* **1976**, *41*, 3609.

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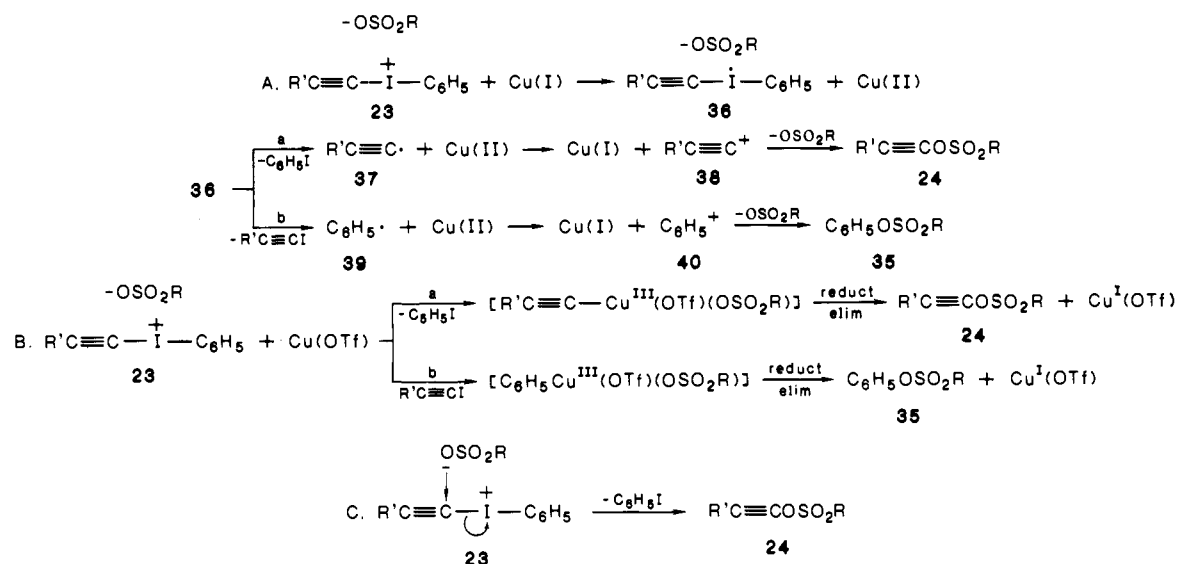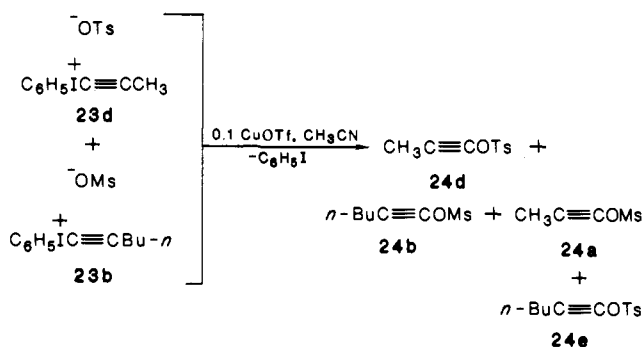
(23) Kochi, J. K. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1.

(24) Beringer, F. M.; Messing, S. *J. Org. Chem.* **1972**, *37*, 2484. Elofson, R. M.; Gadallah, F. F. *Ibid.* **1969**, *34*, 854.

Scheme VII

**Scheme VIII**

Scheme IX

coupling of diaryliodonium salts.[26] Finally, path C involves a nucleophilic acetylenic displacement process known to occur with certain acetylenes with good leaving groups such as haloalkynes.[27]

Path A seems unlikely as both intermediates **38** and **40** are very high in energy, and **38** in particular is some 66 kcal/mol less stable than the methyl cation.[11] Moreover, one would expect some radical coupling products such as either R′C≡C—C≡CR′ from **37** or biphenyl from **39**. No such radical coupling products were observed although small amounts could have escaped detection. Furthermore, since $C_6H_5^+$, although a high-energy intermediate, is 95 kcal/mol more stable[11] than **38**, hence, it should favor path b and formation of the iodoalkynes and phenyl sulfonates contrary to observations.

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(25) Lockhart, T. P. *J. Am. Chem. Soc.* **1983**, *105*, 1940. We are grateful to Dr. Lockhart for suggesting this possibility and bringing it to our attention.

(26) A referee suggested that a related mechanism also involving a Cu(III) species might be in analogy with the recent observations of Ochiai. See:
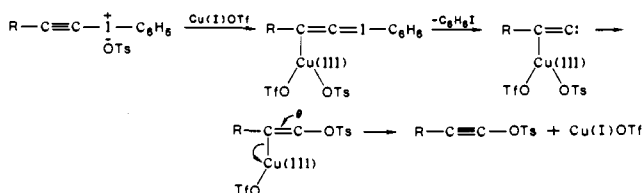
Ochiai, M. et al. *J. Am. Chem. Soc.*, in press.

(27) Miller, S. 1.; Dickstein, J. 1. *Acc. Chem. Res.* **1976**, *9*, 358. Miller, S. 1.; Dickstein, J. 1. In *The Chemistry of the Carbon–Carbon Triple Bond*; Patai, S., Ed.; Wiley-Interscience: London, 1978; Part 2, Chapter 19, pp 813–955.
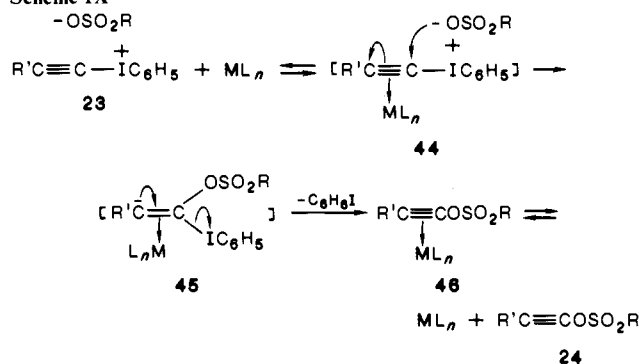
In mechanism B, path a is favored over b due to the greater stability of alkynyl copper compared to aryl copper compounds. However, when using stoichiometric or excess CuOTf one would expect to see alkynyl triflates as well as alkynyl tosylates (or mesylates), yet none were observed.[28]

In order to further delineate the mechanism of formation of **24**, the following experiments were carried out: A crossover experiment was performed as shown in Scheme VIII. Reaction of equal molar amounts of propynyliodonium tosylate **23d** and *n*-hexynyliodonium mesylate **23b** under the usual conditions gave nearly statistical amounts of crossover products **24a**, **24b**, **24d**, and **24e**. This observation is consistent with either the SET mechanism A or the ionic mechanism C and less likely, but not impossible, with mechanism B.
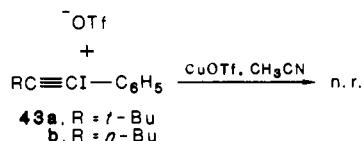
The presence of radical traps, such as O_2, butyraldehyde, or $(CH_3)_3CN=O$, did *not* affect the products nor significantly alter the rates[29] of alkynyliodonium sulfonate decompositions and ester formation. These observations clearly rule out any type of radical chain reaction processes and provide evidence against mechanism A.

Anion exchange of **23g** on triflate-treated Amberlite gave crystalline alkynyliodonium triflate **43**. Treatment of **43** with CuOTf in CH_3CN in the usual manner gave no alkynyl triflate or iodobenzene (as monitored by NMR) even after several weeks.

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(28) In the absence of authentic alkynyl triflates it is possible, however, that they are not stable and hence would decompose and thereby account for their lack of observation. It is also possible that formation of CuOTf is prefered over CuOTs and is driving the reaction to the direction of RC≡COTs rather than RC≡COTf. We are not aware of any relevant thermodynamic data on the relative stabilities of CuOTf, CuOTs, or CuOMs.

(29) Only qualitative rate observations via NMR monitoring were carried out.

The use of forcing conditions (refluxing for several hours), gave only unidentified decomposition products with only traces of C_6H_5I.

$$RC\equiv CI-C_6H_5 \xrightarrow[]{\stackrel{\displaystyle {}^-OTf \;+}{\text{CuOTf, CH}_3\text{CN}}} \text{n.r.}$$

43a, R = *t*-Bu
b, R = *n*-Bu

The above observations are most consistent with a nucleophilic displacement, mechanism C (Scheme VII), that we call a "metal-assisted nucleophilic acetylenic displacement via an addition–elimination process" as outlined in Scheme IX.

The first step in this process involves reversible formation of a metal π-complex **44**. All of the metals found to be active catalysts [Cu(I), Ag(I), and Pd] are known to form π-acetylene complexes.[30] Such complexation withdraws sufficient electron density from a normally electron rich acetylene (a kind of umpolung) to allow the ready addition[31] of even weak nucleophiles, such as tosylates and mesylates, forming **45**. Subsequent loss of the leaving group as the neutral iodobenzene, analogous to the loss of nitrogen from a diazonium ion, results in complexed alkynyl sulfonate **46** that is in equilibrium with the free ester **24**.

This proposed mechanism depends upon and is made possible by two *essential* features. The availability of an excellent "leaving group", namely an iodonium ion, that is probably comparable in reactivity to a diazonium ion and certainly more reactive than the common sulfonate leaving groups (probably including the so called "super leaving groups" of FSO_3^-, $CF_3SO_3^-$ and $C_4F_9SO_3^-$).[32] Secondly, the use of π-complexation and umpolung enable the addition of a weak nucleophile to a normally electron rich acetylene.

The mechanism nicely accounts for the following experimental observations. Metals other than SET agents, i.e., Pd (and to a lesser extent Pt), capable of π-complexation act in a catalytic manner. Crossover is expected and consistent with such an "ionic" mechanism. Radical traps do not affect the process as there are no radicals involved. Most importantly, iodonium triflates **43** do not react because the triflate ion is insufficiently nucleophilic to undergo addition even when "assisted" by electron withdrawal due to π-complexation.

By use of stoichiometric amounts of CuOTf and **43** we have attempted to isolate the analogous intermediate π-complex **44** but to date have not been successful.

Conclusions. We have prepared alkynyl tosylates **11** and mesylates **12** that represent the first known examples of any type of acetylenic esters **7–9**. With the exception of the phenylethynyl species these sulfonates are *stable*, pale yellow oils that were completely identified by spectral and chemical means. Particularly characteristic are the very strong absorptions in the infrared spectrum around 2280 cm^{-1} due to the symmetrically substituted carbon–carbon triple bond and the ^{13}C NMR of the acetylenic carbons centered at 70–90 ppm for the α C and at 40–50 ppm for the β C. X-ray data show the alkynyl iodonium sulfonates **23h** to be 10-I-3 species with a distorted pseudotrigonal bipyramidal (T-shaped) geometry. A metal-assisted nucleophilic acetylenic displacement via an addition–elimination process is proposed as the most likely mechanism for the novel ligand–ligand coupling reaction resulting in alkynyl sulfonates via tricoordinate iodonium species.

The implications of ligand–ligand coupling in main group chemistry, in analogy to their counterparts in organometallic chemistry, as well as the implications of the use of π-complexation in acetylene and olefin chemistry to achieve an umpolung by electron withdrawal are currently under investigation. Likewise, the generality of these methods to the synthesis of the other missing acetylenic esters[33] **7** and **9** and other novel acetylenes as well as the chemistry of these previously unknown alkynyl sulfonates are under active investigation and will be the subject of future reports.

Experimental Section

General Methods. Melting points were obtained with a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 298 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on either a Varian EM-360, EM-390, FT-80, or SC-300 spectrometer. Chemical shifts (^{1}H, ^{13}C) were reported in parts per million (ppm) downfield from internal tetramethylsilane(Me$_4$Si). ^{19}F NMR shift (ppm) were reported relative to internal CFCl$_3$. Chemical ionization mass spectra (CI/MS) were obtained by using CH$_4$ as the ionizing gas on either a Varian Mat 112 mass spectrometer with a Spectroscan 100 data system or a VG Micromass 7070-E double focusing high resolution mass spectrometer operating at 5 kV with a VG Analytical DS 2050 data system. High-performance liquid chromatography (HPLC) was performed by using 3% ethyl acetate in hexanes on a Varian 5000 liquid chromatograph equipped with a Varian CN-10 30 cm × 8 mm MicroPak column, a variable wavelength UV detector, and a Varian model 9176 strip chart recorder. Gas chromatography was performed on a Hewlett Packard 5710 gas chromatograph equipped with a 10 ft × 1/8 in. QF-1 (15%) column, a flame ionization detector, and a Hewlett Packard 3380 A integrator/recorder.

Materials. All commercial reagents were ACS reagent grade and used without further purification. Iodobenzene diacetate was purchased from Aldrich Chemical Company. Acetylenes were purchased from Farchan Laboratories. Authentic tosylate and carboxylate esters unless commercially available were prepared by using established procedures. The THF desiccant (silica bead) was purchased from EM Science. Copper(II) triflate and copper(I) triflate were prepared by the method of Jenkins and Kochi.[12] The CuOTf solution thus prepared was determined to be 0.047 M by placing aliquots into excess ferric chloride and titrating with standard permanganate. Silver triflate and mercuric triflate were prepared analogously to cupric triflate. Silica gel (Davisil) was not activated prior to use.

General Procedure for the Formation of Phenylhydroxyiodonium Sulfonate Salts. Phenylhydroxyiodonium Tosylate (22a). This salt was prepared by the method of Koser and Wettach.[9] A solution of toluenesulfonic acid monohydrate (**21a**) (7.6 g, 40 mmol) in CH$_3$CN (70 mL) was added to a suspension of iodobenzene diacetate (**20**) (6.4 g, 20 mmol) in CH$_3$CN (40 mL) with swirling; a yellow color developed immediately as **20** rapidly dissolved. The yellow color was soon discharged as a white precipitate formed. The mixture was stirred for an additional 30 min. Then the solid was filtered, washed with acetone and with ether, and dried in vacuo to give 6.4 g (88% yield): mp 135–138 °C (lit.[9] mp 135–138 °C). The IR and NMR spectra agreed with literature values.[9,16]

Phenylhydroxyiodonium Mesylate (22b). This salt was prepared from a solution of methanesulfonic acid (4.8 g, 50 mmol) and water (0.9 g, 50 mmol) in CH$_3$CN (10 mL) and a suspension of **20** (8.0 g, 25 mmol) in CH$_3$CN (50 mL) according to the general procedure to give 5.5 g (70% yield) of **22b** as an off-white powder: mp 120–122 °C; IR (KBr) 3420 (br), 1570, 1468, 1437, 1318, 1230, 1190 (strong), 1057 (strong), 1008, 982, 783, 748, 724, 680, 650 cm^{-1}; ^{1}H NMR (60 MHz, Me$_2$SO) δ 9.31 (s, 1 H), 8.34–8.20 (m, 2 H), 7.70–7.61 (m, 3 H), 2.41 (s, 3 H).

General Procedure for the Formation of Phenylalkynyliodonium Sulfonate Salts. Phenylpropynyliodonium Tosylate (23d). This compound was prepared in a thick-walled high-pressure reaction bottle since the alkyne is a gas at room temperature. For other alkynes a round-bottom flask was employed. Propyne (85%, stabilized with allene) (10 mL) was condensed in the reaction vessel at −78 °C and was diluted with CH$_2$Cl$_2$ (50 mL). Then THF desiccant (3 g) and **22a** (3.1 g, 7.9 mmol) were added, and the vessel was flushed with argon and stoppered. The mixture was allowed to warm to room temperature and was stirred magnetically for 20 h dissolving **22a**. The mixture was cooled to −78 °C to relieve the pressure, the stopper was removed, and with stirring the mixture was allowed to warm to room temperature again releasing excess propyne. Then the solution was filtered and concentrated in vacuo to give a yellow oil mixed with a solid. The solid was washed with ether (2 × 10 mL) and chromatographed on silica (20-cm column, 2-cm diameter) with CH$_2$Cl$_2$ elution. After a brown band had eluted, **23d** was eluted with 10% acetone in CH$_2$Cl$_2$ (100 mL) and then 20% acetone. The solvent

(30) *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergammon Press: Oxford, 1982, (Cu, Ag) Vol. 2, Chapter 14 and Vol. 7, Chapter 49; (Pt) Vol. 6, Chapter 39; (Pd) Vol. 6, Chapter 38 and Vol. 8, Chapter 57.

(31) Displacement or substitution by "addition–elimination", rather than direct displacement on the acetylenic carbon by an extremely unlikely S_N2-type process, is, of course, well-known in nucleophilic vinylic substitution (S_NV) reactions. For recent reviews, see: Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7.

(32) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

(33) Stang, P. J.; Böhshar, M.; Lin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7832.

was removed in vacuo to give a yellow oil which gradually crystallized. The solid was washed with a little ether to give 622 mg (19% yield) of **23d** as a white powder: mp 123–127 °C dec; IR (Nujol) 2190, 1222, 1150, 1120, 1028, 997, 986, 860, 823, 742, 685, cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) 7.98, (dd, $J = 2, 8$ Hz, 2 H), 7.65–7.12 (m, 5 H), 7.03 (d, $J = 8$ Hz, 2 H), 2.29 (s, 3 H), 2.06 (s, 3 H).

Phenyl(*n*-butylethynyl)iodonium Tosylate (23e). This salt was prepared from 8.0 g (20 mmol) of **22a** and 10 mL (110 mmol) of 1-hexyne in 50 mL of CH$_2$Cl$_2$ with 5 g of desiccant according to the general procedure. Stirring for 36 h was required to dissolve **22a**. The yield of **23e** was 1.1 g (12%) as a white powder: mp 81–83 °C; IR (Nujol) 2185, 1225, 1180, 1140, 1115, 1028, 1002, 987, 807, 737, 677 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 8.06 (dd, $J = 2, 8$ Hz, 2 H), 7.64 (d, $J = 8$ Hz, 2 H), 7.57–7.30 (m, 3 H), 7.10 (d, $J = 8$ Hz, 2 H), 2.43 (t, $J = 7$ Hz, 2 H), 2.33 (s, 3 H), 1.60–1.12 (m, 4 H), 0.85 (5, $J = 7$ Hz, 3 H).

Phenyl(*sec*-butylethynyl)iodonium Tosylate (23f). This salt was prepared from 2.0 g (5 mmol) of **22a** and 3 mL of 3-methyl-1-pentyne in 125 mL of CH$_2$Cl$_2$. Refluxing overnight followed by standard workup gave 1.2 g (52%) of **23f** as a white powder: mp 86–89 °C (dec); IR (KBr) 2170, 1220, 1150, 1120, 1025, 1000, 810, 740, 680 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.1 (d, 2 H), 7.65–7.25 (m, 5 H), 7.10 (d, 2 H), 2.65 (m, 1 H), 2.35 (s, 3 H), 1.50 (m, 2 H), 1.20 (d, 3 H), 0.95 (t, 3 H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 141.3, 140.1, 133.4, 131.8, 131.6, 128.6, 125.9, 118.4 (Ar), 113.0 (β C), 28.7 (α C), 29.4, 29.2, 21.4, 19.8, 11.6.

Phenyl(*tert*-butylethynyl)iodonium Tosylate (23g). This salt was prepared by the method of Rebrovic and Koser.[10] *tert*-Butylacetylene (9 mL, 73 mmol) and **22a** (8.0 g, 20 mmol) were combined in CHCl$_3$ (50 mL), and the mixture was heated to reflux for 5 h. The resulting solution was concentrated in vacuo, and the residue was washed with ether providing 6.1 g (67% yield) of **23g** as a white powder: mp 129–133 °C dec (lit.[10] mp 137.5–139 °C dec). The IR and ^{1}H NMR spectra agreed with literature[10] data.

Phenyl(phenylethynyl)iodonium Tosylate (23h). This salt was prepared from **22a** (197 g, 5.24 mmol) and phenylacetylene (2.0 mL, 18.2 mmol) in 25 mL of CH$_2$Cl$_2$ with 1 g of desiccant according to the general procedure. The reaction was complete in 15 h, and washing with ether was sufficient to provide 1.47 g (61.14% yield) of **23h** as a white powder: mp 118–124 °C dec (lit.[10] mp 119–122 °C dec). The IR and ^{1}H NMR agreed with literature data.[10] For single-crystal X-ray analysis: in a 50-mL beaker, **23h** was dissolved in about twice the CHCl$_3$ needed for a saturated solution (10 mL). The beaker was placed in a large brown jar containing pentane and was covered with a 150-mL beaker to maintain a saturated atmosphere. After the jar was capped, pentane diffused into the CHCl$_3$ solution causing crystallization of **23h**. The mother liquor was decanted, and the crystals were collected and dried in the air.

Phenylpropynyliodonium Mesylate (23a). This salt was prepared from propyne (15 mL) and **22b** (5.0 g, 15.8 mmol) in 150 mL of CH$_2$Cl$_2$ with 5 g of desiccant. To dissolve **22b**, 24 h were required. The yield of crude **23a** was 1.2 g (35%) after washing with ether. The formation of **23a** was indicated by a band at 2190 in the IR and by the ^{1}H NMR which contained signals at δ 8.2 (m, 2 H), 7.6 (m, 3 H), 2.67 (s, 3 H), 1.70 (s, 3 H).

Phenyl(*n*-butylethynyl)iodonium Mesylate (23b). This salt was prepared from 1-hexyne (5 mL, 55 mmol) and **22b** (5.0 g, 15.8 mmol) in 50 mL of CH$_2$Cl$_2$ with 5 g of desiccant. To dissolve **22b**, 8 h were required. The yield of **23b** was 1.6 g (27%) after column chromatography: mp 88–90 °C; IR (KBr) 3215, 1560, 1200 (br), 1050, 1015, 763, 732, 674 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 8.23 (m, 2 H), 6.60 (m, 3 H), 2.67 (s, 3 H), 2.57 (t, $J = 9$ Hz, 2 H), 1.50 (m, 4 H), 0.90 (t, $J = 9$ Hz, 3 H).

Phenyl(*tert*-butylethynyl)iodonium Mesylate (23c). This salt was prepared from *tert*-butylacetylene (3 mL, 24 mmol) and **22b** (3 g, 9.5 mmol) in 100 mL of CH$_2$Cl$_2$ with 3 g of desiccant according to the general procedure. The reaction was complete in 96 h, and washing with ether was sufficient to provide 2.6 g (72% yield) of **23c** as a white powder: mp 126–127 °C; IR (KBr) 2175, 2140, 1323, 1310, 1200 (br) 1050, 1020, 777, 766, 743, 682, 649 cm^{-1}; ^{1}H NMR (60 MHz, CDCl$_3$) δ 8.25 (m, 2 H), 7.63 (m, 3 H), 2.70 (s, 3 H), 1.25 (s, 9 H).

General Procedure for the Formation of Phenylalkynyliodonium Triflate Salts. Phenyl(*tert*-butylethynyl)iodonium Triflate (43a). A triflate anion exchange resin was prepared by treating Amberlite IRA 401s resin repeatedly with aqueous triflic acid (TfOH) (8 M) until the solution tested negative for chloride with AgNO$_3$ (0.1 M). The resin was rinsed with copious amounts of distilled water between TfOH treatments. Finally, the resin was rinsed with water until the rinsings tested neutral by litmus paper. A column was prepared with 10 mL of wet resin in 20% aqueous methanol and **23g** (100 mg, 0.22 mmol) in 50% aqueous methanol (1 mL) was placed on the column. Elution with 20% aqueous methanol (30 mL) and concentration of the eluent provided 84.5 mg of **43a** (88% yield) as a white crystalline solid after drying in vacuo: mp

125–135 °C; IR (Nujol) 2180, 2145, 2184, 1217, 1157, 1022, 985, 738, 675, 633 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 8.0 (m, 2 H), 7.5 (m, 3 H), 1.26 (s, 9 H); ^{13}C NMR (80 MHz, CDCl$_3$) δ 133.9, 132.5, 132.3, 117.5, 115.2, 77.8, 29.9, 12.8; ^{19}F NMR (74.8 MHz, CDCl$_3$) δ 78.6 ppm upfield from internal CFCl$_3$.

Phenyl(*n*-butylethynyl)iodonium Triflate (43b). This salt was prepared from (274 mg, 0.600 mmol) according to the general procedure. The yield of **43b** was 233 mg (85%); mp 64–68 °C; IR (Nujol) 2185, 2170, 1230, 1170, 1022, 988, 741, 677, 634 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 8.0 (dd, $J = 2, 8$ Hz, 2 H), 7.67–7.32 (m, 3 H), 2.54 (t, $J = 6$ Hz, 2 H), 1.66–1.14 (m, 4 H), 0.86 (t, $J = 6$ Hz, 3 H).

General Procedure for the Decomposition of the Phenylalkynyl-iodonium Sulfonate Salts. Formation of 1-Propynyl Tosylate (24d). This ester was obtained when **23d** (600 mg, 1.45 mmol) was decomposed in a solution of CuOTf (0.047 M in CH$_3$CN, 20 mL, 1 mmol). The course of the reaction was followed by ^{1}H NMR, observing the disappearance of the signal at δ 8.2–8.0 as new peaks grew in between δ 8.0 and 7.6. The reaction was complete in 2 h. The solvent was removed in vacuo, and the residue was taken up in 1:1 CH$_2$Cl$_2$/hexanes, filtered, concentrated, and chromatographed on silica (20-cm column, 2-cm diameter). The column was eluted with hexanes, 10%, 20%, 30%, and 40% CH$_2$Cl$_2$ in hexanes (50 mL each). The fractions containing **24d** were combined and concentrated. The residue was distilled (Kugelrohr, 100 °C, 0.05 mmHg) to give 116 mg of **24d** (38% yield) as a pale yellow oil: IR (neat) 2280, 1595, 1400, 1220, 1190, 1180, 810 cm^{-1}; ^{1}H NMR (90 MHz, CD$_2$Cl$_2$) δ 7.7 (d, 2 H), 7.3 (d, 2 H), 2.3 (s, 3 H), 1.5 (s, 3 H); ^{13}C NMR (300 MHz, CD$_2$Cl$_2$) δ 148.2, 130.9, 130.6, 129.7, 77.9, 44.1, 22.0, 1.6; MS (CI, CH$_4$), 221 (MH$^+$, 100.0), 155 (30.7), 139 (35.3). Anal. Calcd for C$_{10}$H$_{10}$O$_3$S: C, 57.14; H, 4.76; S, 15.23. Found: C, 57.08; H, 4.80; S, 15.32.

***n*-Butylethynyl Tosylate (24e).** Iodonium tosylate **23e** (338 mg, 0.74 mmol) was decomposed in 4 mL of 0.047 M CuOTf (0.1 mmol) according to the general procedure. The yield of **24e** was 165 mg (88%) after distillation (Kugelrohr, 130 °C, 0.05 mmHg): IR (neat) 2275, 1595, 1400, 1205, 1190, 1180, 810 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 7.8 (d, 2 H), 7.3 (d, 2 H), 2.4 (s, 3 H), 2.1 (m, 2 H), 1.5–0.8 (m, 7 H); ^{13}C NMR (300 MHz, CD$_2$Cl$_2$) δ 148.2, 130.8, 130.6, 129.8, 79.2, 48.4, 31.1, 22.1, 22.0, 16.9, 13.7; MS (CI, CH$_4$), 253 (MH$^+$, 11.2), 251 (11.5), 155 (100.0), 139 (60.7). Anal. Calcd for C$_{13}$H$_{16}$O$_3$S: C, 61.87; H, 6.40; S, 12.70. Found: C, 62.89; H, 6.50; S, 11.84.

***sec*-Butylethynyl Tosylate (24f).** The decomposition of **23f** (2.0 g, 4.4 mmol) was performed in 25 mL of CH$_3$CN by using AgOTs (0.05 g, 2 mmol) as the catalyst. The reaction was complete in approximately 4 h. Silica gel chromatography with 90:10 hexanes/CH$_2$Cl$_2$ gave 0.80 g (72%) of **24f** as a colorless oil which solidified with slight cooling: mp 26–27 °C; IR (neat) 2265, 1595, 1400, 1220, 1195, 1180, 810 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 7.8 (d, 2 H), 7.3 (d, 2 H), 2.4 (s, 3 H), 2.2 (m, 1 H), 1.4–0.8 (m, 8 H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 147.7, 129.9, 129.7, 128.9 (Ar), 79.2 (α C), 51.9 (β C), 29.8, 26.2, 21.8, 20.6, 11.5. Anal. Calcd for C$_{13}$H$_{16}$O$_3$S: C, 61.88; H, 6.39; S, 12.71. Found: C, 61.58; H, 6.23 S, 12.52.

***tert*-Butylethynyl Tosylate (24g).** The decomposition of **23g** (2.0 g, 4.4 mmol) was effected by AgOTf (100 mg, 0.39 mmol) in CH$_3$CN (10 mL). The reaction was essentially complete in 20 h. The yield of **24g** was 412 mg (37%) after Kugelrohr distillation (130 °C, 0.15 mmHg): IR (neat) 2280, 1595, 1400, 1195, 1180, 810 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 7.8 (d, 2 H), 7.3 (d, 2 H), 2.4 (s, 3 H), 1.3 (s, 9 H); ^{13}C NMR (80 MHz, CD$_2$Cl$_2$) δ 147.6, 130.3, 130.1, 129.5, 78.8, 56.2, 31.1, 26.7, 21.2; MS (CI, CH$_4$), 253 (MH$^+$, 2.0), 237 (19.7), 155 (100.0), 139 (10.8). Anal. Calcd for C$_{13}$H$_{16}$O$_3$S: C, 61.60; H, 6.82; S, 12.65. Found: C, 62.26; H, 6.61; S, 12.36.

Phenylethynyl Tosylate (24h). The decomposition of **23h** (1.0 g, 2.1 mmol) in 0.047 M CuOTf (50 mL, 2.3 mmol) according to the general procedure required 4 h to complete due to the insolubility of **23h** in CH$_3$CN. Because of the instability of **24h** when neat, it was crystallized from the chromatography eluent at −78 °C after concentrating the solution to about half volume in vacuo at 20 °C. The flocculent white solid was cold filtered by suction and most of the solvent was removed on a vacuum line, then it was redissolved for spectral analysis or chemical transformation before it warmed to room temperature: IR (CD$_2$Cl$_2$) 3060, 2920, 2260, 1595, 1400, 1195, 1175, 810 cm^{-1}; ^{1}H NMR (80 MHz, CD$_2$Cl$_2$) δ 8.0 (d, 2 H), 7.5 (d, 2 H), 7.3 (s, 5 H), 2.4 (s, 3 H); ^{13}C NMR (300 MHz, CD$_2$Cl$_2$) δ 148.3, 131.9, 130.5, 129.4, 129.0, 128.8, 128.5, 120.8, 87.2, 48.2, 21.7; MS (CI, CH$_4$), 273 (MH$^+$, 3.9), 155 (19.3), 139 (25.6).

1-Propynyl Mesylate (24a). The decomposition of **23a** (1.9 g, 5.6 mmol) in 130 mL of 0.044 M CuOTf (5.7 mmol) in acetonitrile according to the general procedure required 6 h to complete. The yield of **24a** was 450 mg (60%) as a pale yellow oil: IR (neat) 3020, 2935, 2275, 1375, 1190, 965, 800, 775, 660 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 3.3

(s, 3 H), 2.8 (s, 3 H); ^{13}C (80 MHz, CD$_2$Cl$_2$) δ 77.1, 44.2, 36.8, 1.5; MS (EI), 134 (M$^+$, 13.8), 119 (41.8), 106 (26.9), 79 (78.4).

n-Butylethynyl Mesylate (24b). Iodonium mesylate **23b** (3.4 g, 8.9 mmol) was decomposed in 250 mL of 0.044 M CuOTf (11 mmol) in acetonitrile according to the general procedure. The reaction was complete in 4 h. The yield of **24b** was 850 mg (54%) as a pale yellow oil: IR (neat) 2265, 1380, 1325, 1180, 965, 815, 775, 650 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 3.3 (s, 3 H), 2.2 (m, 2 H), 1.5–0.8 (m, 7 H); ^{13}C NMR (90 MHz, CDCl$_3$) δ 78.3, 48.3, 36.7, 30.8, 21.9, 16.7, 13.5; MS (EI), 133 (M$^+$ − C$_3$H$_7$, 28.8), 98 (11.8), 97 (10.6), 79 (31.3), 64 (100.0).

***tert*-Butylethynyl Mesylate (24c).** The decomposition of **23c** (1.5 g, 3.9 mmol) was effected by refluxing in 100 mL of 0.044 M CuOTf (4.4 mmol) in acetonitrile for 18 h. The yield was 350 mg (50%) as a pale yellow oil: IR (neat) 2280, 1400, 1240, 1180, 970, 920, 800, 770, 660 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 3.3 (s, 3 H), 1.2 (s, 9 H); ^{13}C NMR (80 MHz, CDCl$_3$) δ 77.9, 65.1, 63.5, 31.0, 26.6; MS (EI), 176 (M$^+$, 6.0), 161 (52.8), 83 (36.0), 82 (43.0), 79 (20.8), 64 (11.5), 57 (16.1), 41 (100.0).

Decomposition of Two Iodonium Salts. The Classical Crossover Experiment. Phenylpropynyliodonium tosylate (**23d**) (20.6 mg, 0.050 mmol) and phenyl-(*n*-butylethynyl)iodonium mesylate (**23b**) (20.1 mg, 0.053 mmol) were dissolved in 0.047 M CuOTf (1 mL, 0.05 mmol). After 2 h, decomposition was complete as judged by NMR. HPLC analysis by direct injection of the product mixture showed a 1:1 mixture of *n*-butylethynyl tosylate (**24e**), identified by coinjection of an authentic sample and propynyl tosylate (**24d**). A control reaction run at the same time containing only **23d** (20.6 mg, 0.050 mmol) in 1.0 mL of 0.047 M CuOTf showed the yield of **24d** was halved in the reaction for the two salts. Gas chromatographic analysis of the crossover product mixture by direct injection showed approximately equal amounts of propynyl mesylate (**24a**), identified by coinjection of authentic **24a**, and *n*-butylethynyl mesylate (**24b**). Another control reaction of just **23b** (20.1 mg, 0.053 mmol) in 1.0 mL of 0.047 M CuOTf showed that the yield of **24b** was halved in the reaction of the two salts.

Decomposition of an Iodonium Salt in the Presence of Radical Traps. A solution of phenyl-(*n*-butylethynyl)iodonium tosylate (**23e**) in CH$_3$CN (4 mL) was mixed with 0.047 M CuOTf (0.8 mL, 0.004 mmol). The resulting solution was divided into 4 equal parts (1.0 mL each). One part (reaction 1) was mixed with 1,1-dimethylnitrosoethane (21.1 mg, 0.242 mmol), another (reaction 2) with butyraldehyde (19.7 mg, 0.274 mmol), oxygen was bubbled through reaction 3, and reaction 4 was used as a control. Reaction 1 was the slowest, requiring about twice as long as the control, reaction 2 was intermediate, and reaction 3 was almost as fast as the control which required 4.5 h. The yield of *n*-butylethynyl tosylate (**24e**) was virtually the same in each reaction as judged by HPLC analysis of the product mixtures directly. Also, no difference could be seen qualitatively in the NMR spectra of the crude product mixtures or in the IR spectra of work-up products, which all show a mixture of iodobenzene and **24e**. The workup consisted of concentration, elution through a 1-in silica column with CH$_2$Cl$_2$, and concentration of the eluent.

An Attempt To Decompose an Iodonium Triflate. Compound **43b** (160 mg, 0.37 mmol) was dissolved in 0.047 M CuOTf (2 mL, 0.1 mmol). Very little change had occurred after several weeks of monitoring by NMR. After this time, refluxing resulted in dark decomposition products with only small amounts of C$_6$H$_5$I identified.

Determination of Catalyst Effectiveness. A 0.09 M stock solution of **23d** in CH$_3$CN was prepared, and 1.0 mL of this solution was mixed with 1.0 mL of each of the following reagents dissolved in CH$_3$CN and the reactions monitored by NMR. (The approximate time required for decomposition is given in parentheses after each reagent): 0.014 M CuOTf (2 h), 0.014 M Cu(OTf)$_2$ (20 h), 0.014 M Cu(OAc)$_2$ (20 h), BF$_3$·Et$_2$O (no reaction), 0.007 M AgOTf (3 h), 0.006 M Pt(PPh$_3$)$_4$ (7 days), 0.008 M Pd(PPh$_3$)$_4$ (1 h). After the reaction was complete, the solvent was evaporated, and the residue was chromatographed on silica (1-in column, CH$_2$Cl$_2$ elution). The eluent was concentrated, and the product was analyzed by IR. In each case this showed a mixture of iodobenzene and propynyl tosylate (**24d**). Phenyl-*tert*-butylethynyl-iodonium tosylate (**23g**) (27.2 mg, 0.06 mmol) was dissolved in CH$_3$CN (1 mL) and mixed with 0.047 M CuOTf (1 mL). After 10 days, only about half of **23g** had reacted.

Methanolysis of *n*-Butylethynyl Tosylate (24e). The tosylate (**24e**) (0.5 g, 2.0 mmol) was dissolved in methanol (50 mL) and stirred with K$_2$CO$_3$ (0.5 g, 4.7 mmol) for 15 min. The solvent was distilled, and the residue was divided between ether and water. The ether part was extracted with water and brine and then dried with K$_2$CO$_3$. The ether was removed by distillation, and the residue was distilled (Kugelrohr, 154 °C, 1 atm) to give 192 mg of methyl caproate (74% yield). The IR and NMR spectra were identical with the spectra of an authentic sample, and GC analysis indicated that it was the same compound by coinjection. The pot residue was mostly methyl tosylate as judged by comparison of the IR and NMR spectra of an authentic sample.

Hydrogenation of *n*-Butylethynyl Tosylate (24e). The tosylate **24e** (160 mg, 0.63 mmol) was dissolved in petroleum ether (bp 30–60 °C) (20 mL) and stirred with 10% Pd on C (37 mg) for 5 days under an atmosphere of hydrogen and then for 1 day with an additional 0.5 g of catalyst. The catalyst was filtered and washed with acetone. (Some irreversible absorption of substrate onto the catalyst was evident by HPLC analysis of the petroleum ether solution.) The solution was dried with K$_2$CO$_3$, filtered, and analyzed by HPLC, which showed several components. The desired product was identified by coinjection of an aliquot with authentic *n*-hexyl tosylate. This component was separated by preparative HPLC to give 32 mg of *n*-hexyl tosylate (20% yield), which was identical with the authentic compound by IR, NMR, and HPLC coinjection.

X-ray Crystallography of Phenyl(phenylethynyl)iodonium Tosylate (23h). A colorless, plate-shaped crystal having dimensions 0.18 × 0.25 × 0.29 mm was mounted on the tip of a glass fiber, covered with epoxy, allowed to dry, then set onto a goniometer, and transferred to a Syntex R 1 bar automated diffractometer. Determination of approximate unit cell parameters, the orientation matrix, and crystal quality (the last via axial photographs) was carried out as previously described.[34] A unique set of data was collected at the maxima scan rate (24°/min in 2θ) 2θ = 18 to 40°. Careful inspection of the data led to the selection of 13 reflections to determine accurate cell parameters via a least-squares procedure.

A unique set of data consisting of $0 < h < 19$, $0 < k < 11$, and $-19 < l < 19$ with 2θ max = 50; Mo Kα = 0.71073, highly oriented graphite monochromator, three standard reflections measured every 97 reflections. A total of 3446 unique reflections were collected.

Computations were performed on the University of Utah, College of Science DEC-20 computer by using SHELX-76. Their analytical scattering factors for neutral atoms[34] were corrected for both the real and the imaginary components of anomalous dispersion.[35]

The structure was solved via a three-dimensional Patterson synthesis which readily yielded the position of the iodine atom. A series of difference-Fourier syntheses revealed all remaining non-hydrogen atoms. Refinement was continued by using anisotropic thermal parameters for I, S, and O atoms. An attempt was made to give all carbon atoms anisotropic thermal parameters; however, due to the paucity of observed ($I > 2.5\sigma(I)$) data this was unfeasible. Hydrogen atoms were placed into calculated positions with d(C–H) = 0.95[36] and idealized geometries (either 3p[36] for methylhydrogens or 5p[36] for aromatic hydrogens). Final R factors are $R = 0.0784$, $R_{is} = 0.0803$ with $R = \sum(|F_o - F_c|)/\sum F_o$, $Rw = \sum|F_o - F_c|w^{1/2}/\sum F_a w^{1/2}$, and $w = 1.5942/[\sigma^2(F) + 0.0056F^2]$ for reflections with $I \geq 2.5\ \sigma(I)$. The largest peak on a final difference Fourier was 0.97 e$^-$/Å[36] near I.

Supplementary Material Available: Details of X-ray data: observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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