C). Anal. Calcd for $C_{31}H_{24}O$: C, 90.26; H, 5.86. Found: C, 90.3; H, 6.0.

Photochemical Isomerization of Dianthrylpropanone 6 To Give 17 and 18. A. By Direct Excitation. A solution of **6** (50 mg) in methylene chloride (150 mL) at 14 °C under argon was irradiated with wavelengths >400 nm for 30 min. Vacuum evaporation of solvent gave a colorless crystalline residue, which was analyzed by ^{1}H NMR and found to consist of the [4 + 4] cyclomer **17** and two isomeric [4 + 2] cyclomers, **18a** and **18b**, in an approximate ratio of 8:1:1. Recrystallization of the crude residue from boiling methylene chloride solution by precipitation with hexane gave the [4 + 4] cyclomer **17** as a colorless crystalline precipitate, which was washed with ether. The crystals turn yellow at about 200 °C, and they melt (dec) around 275–290 °C. ^{1}H NMR (of **17**) 7.31–6.76 (m, 16), 4.65 (q, J = 7.4 Hz, 1), 4.59 (d, J = 11.3 Hz, 1), 4.54 (d, J = 11.3 Hz, 1), 1.89 (d, J = 7.4 Hz, 3). Anal. Calcd for $C_{31}H_{22}O$: C, 90.39; H, 5.41. Found: C, 90.40; H, 5.41.

B. Biacetyl-Sensitized Isomerization of 6 To Give 18. A solution of **6** (20 mg) and biacetyl (800 mg) in benzene (120 mL) was irradiated under argon at 10 °C with light of wavelengths >420 nm. In order to retain **6** at low concentration, three additional 20-mg portions of **6** were added in 20-min intervals. After a total irradiation time of 80 min, the solvent was removed by vacuum evaporation. The oily residue thus obtained was analyzed by ^{1}H NMR and found to consist of **17**, **18a**, and **18b** in an approximate ratio of 3:10:7. The residue crystallized upon treatment with ether. Two recrystallizations from a boiling methylene chloride/methanol mixture gave 30 mg of **18a** as colorless crystals (mp 230–233 °C). Anal. Calcd for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.67; H, 5.35. The combined mother liquors of **18a** were chromatographed on silica gel/toluene. ^{1}H NMR analysis revealed the eluate to consist of a mixture of **17** (13%), **18a** (8%), and **18b** (79%). Isomers **18a** and **18b** are characterized and distinguishable by the ^{1}H NMR data in Chart II (proton denotation is as shown above for 10a).

Photolysis of Dianthrylcyclopropenone 7 To Give 1,2-Di-9-anthrylacetylene (19). A solution of **7** (100 mg) in toluene (180 mL) under argon was irradiated at 30 °C for 30 min. Vacuum evaporation of solvent gave an orange-red crystalline residue, which was suspended in a little methylene chloride. Filtration gave 90 mg (97%) of **19** as orange-red, needle-shaped crystals, mp >350 °C. Both the color and the melting point of **19** deserve comment. When **19** was first prepared by a Wittig-type reaction, it was found to form orange-red crystals (from benzene) which decomposed around 310 °C.[22] We have previously prepared **19** by photolysis of **7** in methylene chloride and obtained needle-shaped orange-red crystals (mp >350 °C) by slow recrystallization from methylene chloride at room temperature. Acetylene **19** obtained in this fashion was used in an X-ray diffraction analysis.[28] We now find that recrystallization of **19** from a stirred hot methylene chloride solution gives a "cubic" modification of lemon-yellow crystals which melt around 325 °C. ^{1}H NMR 8.92 (d, J = 8.6 Hz, 4), 8.52 (s, 2), 8.09 (d, J = 8.8 Hz, 4), 7.68–7.54 (m, 8).

Acknowledgment. We are gratefully indebted to Mr. Gunnar Svensson for technical assistance, to Dr. Kjell Ankner of Hässle AB, Mölndal, for running the ^{13}C spectrum of **14a**, and to Dr. Bernd Ruge of BASF AG, Ludwigshafen, West Germany, for providing the phase-transfer catalyst.

Registry No. **1a**, 3162-57-0; **1b**, 110373-64-3; **1c**, 110373-66-5; **1c** (tetrahydro deriv), 110373-85-8; **1d**, 110373-68-7; **1e**, 110373-70-1; **1f**, 110373-72-3; **2a**, 3849-11-4; **2b**, 110373-65-4; **2c**, 110373-67-6; **2d**, 110373-69-8; **2e**, 110373-71-2; **2f**, 110373-73-4; **5**, 102725-05-3; **6**, 110373-74-5; **7**, 78594-10-2; **8**, 110373-75-6; **9**, 102725-09-7; **10a**, 110373-76-7; **11**, 110373-77-8; **12a**, 110373-78-9; **14a**, 110373-79-0; **15a**, 110373-80-3; **15b**, 110373-82-5; **16**, 110373-81-4; **17**, 110391-23-6; **18a**, 110373-83-6; **18b**, 110391-24-7; **19**, 20199-19-3; tetrachlorocyclopropene, 6262-42-6; anthracene, 120-12-7.

(28) Becker, H.-D.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1985**, *38*, 1567.

Electrophilic Additions to Alkynyl Tosylates. Formation of Vinyl 1,1-(Bis esters) and Related Compounds. X-ray Structure Determination of (*E*)-1-Chloro-1-(tosyloxy)-3,3-dimethyl-1-butene†

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The reaction of alkynyl tosylates, RC≡COTs, R = *t*-Bu, *sec*-Bu, with a variety of electrophiles, HCl, CF_3COOH, CF_3SO_3H, $ArSO_3H$, and H_3O^+, in CH_2Cl_2 is reported. Only regio- and stereospecific syn-monoaddition products were observed, yielding vinyl 1,1-(bis esters) and related compounds in good yields. The single-crystal X-ray data of the HCl adduct to *t*-BuC≡COTs is reported. These results and their mechanistic implications are discussed.

Electrophilic addition to alkynes is an important, well-established reaction in synthesis and industrial processes.[2] A variety of alkynes readily add diverse electrophiles under differing reaction conditions. Acid addition and acid-catalyzed hydration of functionalized alkynes, due to the resulting regio- and stereochemistry and the formation of highly functionalized alkynes, are particularly valuable and interesting.[2]

Recently, we reported[3] the preparation of previously unknown alkynyl tosylates and mesylates. As part of our ongoing studies[4] on the reactions of these novel acetylenic

† Dedicated to Professor George A. Olah on the occasion of his 60th birthday.

(1) Abstracted in part from the Ph.D. Dissertation of K. A. Roberts, The University of Utah, 1988.

(2) Viehe, H. G. *Chemistry of Acetylenes*; Marcel Dekker: New York, 1969. De la Mare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*; Elsevier: Amsterdam, 1982. Patai, S. *The Chemistry of the Carbon-Carbon Triple Bond*; Wiley: New York, 1978.

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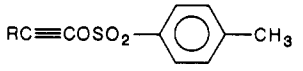
0022-3263/87/1952-5213$01.50/0

Table I. Summary of Acid Additions to Alkynyl Tosylates 1a and 1b

compd	acid	T, °C (rctn, time)	adduct	% yield	ppm ($CDCl_3$), HC=C
1a	HCl(g)	−20 (10 min)	t-BuCH=C(Cl)OTs (2a)	99	5.30
1b	HCl(g)	−20 (10 min)	sec-BuCH=C(Cl)OTs (2b)	99	5.20
1a	TsOH	25 (15 h)	t-BuCH=C(OTs)$_2$ (3a)	99	4.85
1b	TsOH	25 (15 h)	sec-BuCH=C(OTs)$_2$ (3b)	99	4.85
1a	m-$NO_2C_6H_4SO_3H$	25 (15 h)	t-BuCH=C(OTs)$OSO_2C_6H_4NO_2$-m (4a)	99	5.10
1b	m-$NO_2C_6H_4SO_3H$	25 (15 h)	sec-BuCH=C(OTs)$OSO_2C_6H_4NO_2$-m (4b)	99	5.05
1a	CF_3SO_3H	0 (10 min)	t-BuCH=C(OTs)OTf (5a)	60	5.25
1b	CF_3SO_3H	0 (10 min)	sec-BuCH=C(OTs)OTf (5b)	40	5.10
1a	CF_3CO_2H	25 (1 h)	t-BuCH=C(OTs)$OCOCF_3$ (6a)	85	5.10
1b	CF_3CO_2H	25 (1 h)	sec-BuCH=C(OTs)$OCOCF_3$ (6b)	50	5.00

esters, we report the results of the addition of a variety of hydrogen acids in CH_2Cl_2 to *tert*-butylalkynyl and *sec*-butylalkynyl tosylates (**1a** and **1b**, respectively) as prototypes of these new acetylenic sulfonate esters.



1a, R = *t*-Bu
b, R = *sec*-Bu

Results and Discussion

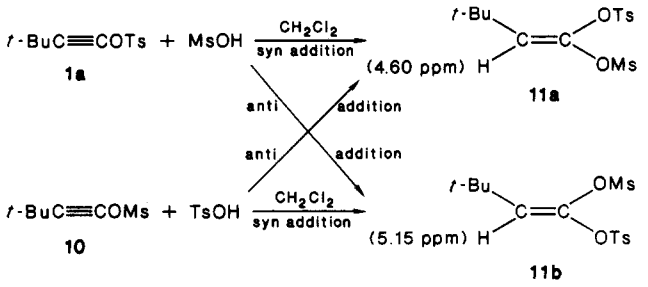
Addition of Hydrochloric, Sulfuric, and Trifluoroacetic Acids. A variety of hydrogen acids (HCl, $ArSO_3H$, CF_3SO_3H, and CF_3CO_2H) readily add to alkynyl tosylates 1 in CH_2Cl_2 under mild conditions (Table I). The reaction is quantitative in all cases[5] with only a *single* isomer being observed and isolated. Evidence for a single isomer includes the very characteristic vinyl proton resonance (Table I) and the single resonances for both the tosyl methyl and the *tert*-butyl methyl groups in both the ^1H and ^{13}C NMR.

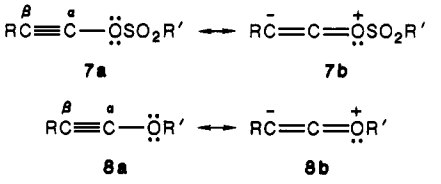
Adducts **3–6**, whose structures are given in Table I, are diesters of alkene-1,1-diols. Although a variety of ketene acetals (bis acetals of enediols) are well-known,[6] disulfonates **3–5** and mixed diesters **6** are to our knowledge unknown. Adducts **2–4** are remarkably stable and are not affected by heat, light, water, or oxygen. Mixed esters **6a** and **6b** are easily isolated and characterized, but decompose after several hours at room temperature, whereas the mixed sulfonate **5a** and **5b** decompose within minutes at room temperature or after several days at ~0 °C.

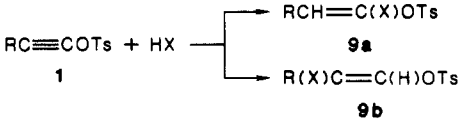
Interestingly, weaker acids such as CH_3COOH, $(EtO)_2P(O)OH$, and HN_3 do not add to these novel alkynyl tosylates even in refluxing chloroform, although HOAc[7] and HN_3[8] are both known to add to the more electron-rich alkynyl ethers (RC≡C–OR′) albeit in more polar solvents.

Regio- and Stereochemistry. The isolation of a *single* isomer in all additions was at first a surprise. Sulfonates, despite their electron-withdrawing nature by induction ($MeSO_3$, σ_I = +0.61; p-$CH_3C_6H_4SO_3$, σ_I = +0.54), are known[9] to be electron donating by resonance ($MeSO_3$, σ_R = −0.28; p-$CH_3C_6H_4SO_3$, σ_R = −0.21). The acetylenic group in alkynyl sulfonates is, in fact, electron rich. This is shown by the considerable upfield shift[3] of the β-carbon in the ^{13}C NMR, due to the contribution of the resonance hybrid **7b** in analogy to alkoxyalkynes 8 (CH_3O; σ_I = +0.21, σ_R = −0.47). Hence, one would expect any electrophilic addition to 1 to be at least regioselective and perhaps regiospecific in favor of **9a**. It is much more difficult to predict a priori the stereochemistry of addition as both syn and anti additions are possible and known.[2] In fact, the relatively high-field location, together with the coupling (in the case of **2b**, **3b**, **4b**, **5b**, and **6b**) of the vinylic proton (Table I and the Experimental Section) readily confirmed the regiochemistry as being exclusively **9a**, as expected.

Scheme I







It is not trivial to assign the stereochemistry of trisubstituted olefins, particularly when only one of the two possible geometric isomers is available. Hence, we needed a way of getting both geometric isomers of an adduct and a definite way of assigning stereochemistry. The latter was readily accomplished by X-ray crystallography and the former as follows.

As addition occurs stereospecifically, the addition of CH_3SO_3H to **1a** should give one isomer, **11a**. The addition of TsOH to the corresponding mesylate **10** should give the opposite isomer **11b**, assuming syn addition (or vice versa if anti addition occurs) as shown in Scheme I.

Indeed only a *single* isomer was obtained from each reaction, with the CH_3SO_3H addition product **11a** having a vinylic proton signal at 4.60 ppm in $CDCl_3$ and the $CH_3C_6H_5SO_3H$ addition product **11b** at 5.15 ppm.

Since the 1,1-ditosylates **3a** and **3b** both had a vinylic proton signal at 4.85 ppm (Table I) and **11a** at 4.60 ppm, this strongly indicates that a syn tosylate provides some

(4) Stang, P. J.; Roberts, K. A. *J. Am. Chem. Soc.* **1986**, *108*, 7125.
(5) Adducts **5** and **6** are somewhat unstable and hence losses occur during workup. However, the IR and NMR spectra of the crude reaction mixtures show only a single product.
(6) Matsumoto, K.; Sera, A. *Synthesis* **1985**, 1017. Brownbridge, P. *Ibid.* **1983**, 1.
(7) Zwanenburg, B.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 879.
(8) Sinnema, Y. A.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1955**, *74*, 901.
(9) Stang, P. J.; Anderson, A. G. *J. Org. Chem.* **1976**, *41*, 781.

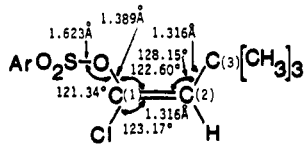


Figure 1. Selected structural data of **2a**.

Table II. Summary of Crystallographic Data for 2a

molecular formula	$C_{13}H_{17}O_3SCl$
molecular weight	288.81
crystal system	monoclinic
space group	$P2_1/n$
cell dimensions:	
a, Å	8.466 (1)
b, Å	6.930 (1)
c, Å	24.943 (6)
β, deg	97.28 (2)
Z	4
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	5.7
$R_w = [\Sigma W\|\|F_o\| - \|F_c\|\|^2/W\|F_o\|^2]^{1/2}$	5.5

shielding and results in an upfield shift of 0.2–0.4 ppm for the vinylic proton. As *all* other addition products had their vinylic proton absorption below 5.00 ppm (5.05–5.30 ppm, Table I) in analogy with the 5.15 ppm for **11b**, this indicates that addition is preferentially syn and all adducts in Table I are the result of syn addition. However, to obtain conclusive proof of this hypothesis a single-crystal X-ray determination was undertaken for one of the adducts in Table I.

X-ray Structure Determination of Adduct 2a. Of all the adducts, **2–6**, as well as **11**, only **2a**, **3a**, **4a**, and **4b** were solid at room temperature. Compound **4a** formed "twin" crystals repeatedly and was unsuitable for crystallography. Since **3a** and **3b** have no stereochemistry, we had no choice but to work with **2a**. Suitable crystals of **2a** can easily be grown from hexane by slow evaporation. The relevant crystal and structural data for **2a** are summarized in Tables II and III. The salient structural features and atom numbering are given in Figure 1. The ORTEP view and related data are included in the supplementary material. The X-ray structure clearly and unambigiously establishes the *E* geometry for **2a** and hence addition of HCl (and by analogy, with support by NMR data, all other electrophiles) must occur in a syn fashion. The remainder of the structural features of **2a** are unexceptional. In order to accommodate the bulky *tert*-butyl group and the tosylate on the same side, the molecule experiences small distortions: the dihedral angle between the *t*-Bu and OTs about the double bond is ~4° and the TsOC=C and C=C-*t*-Bu bond angles open up to 122.6° and 128.1°, respectively. All other structural features of **2a** are in the normal range. This indicates that the steric bulk about the double bond is not sufficiently demanding to cause serious distortions.

Acid-Catalyzed Hydration. Acid-catalyzed hydrations of alkynes are among the oldest known reactions of acetylenes,[2] hydration of propyne to acetone having been reported in the 1870s.[10]

Previously we have demonstrated[3] that the reaction of **1** with CH_3O^-/CH_3OH proceeds via S–O cleavage to give methyl esters (via the intermediate ketene) along with CH_3OTs. In contrast, as expected from the known[11,12] behavior of alkynyl ethers, alkynyl tosylates **1** gave

Table III. Selected Structural Data for 2a

Bond Angles, Deg

from	through	to	angle
O1	S	C7	102.28 (24)
C1	O1	S	121.34 (35)
C2	C1	O1	122.60 (53)
C2	C1	Cl	123.17 (48)
O1	C1	Cl	113.87 (39)
C1	C2	C3	128.15 (54)

Interatomic Distances, Å

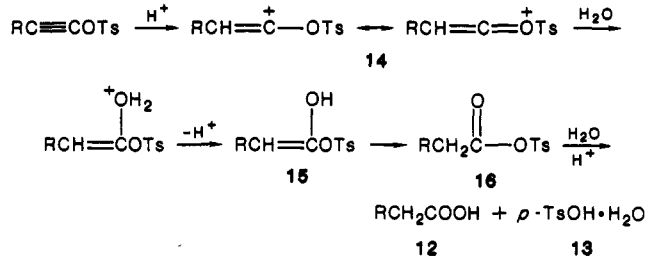
from	to	distance
Cl	C1	1.737 (6)
S	O1	1.623 (4)
O1	C1	1.389 (6)
C1	C2	1.316 (7)
C2	C3	1.504 (7)

Torsion Angles, Deg

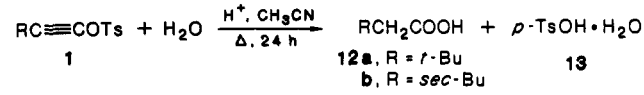
atom 1	atom 2	atom 3	atom 4	angle[a]
S	O1	C1	C2	−117.41
Cl	C1	C2	C3	175.93
O1	C1	C2	C3	3.96

[a] No standard deviation calculated.

Scheme II



quantitative yields of the respective carboxylic acids **12** and hydrated toluenesulfonic acid **13**.



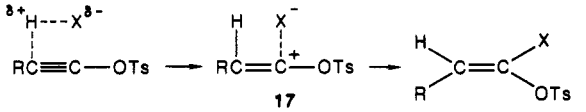
Mechanistic Considerations. Although based only on products and analogy, a basic mechanism can be proposed. It is reasonable to assume that hydration in the polar aqueous acetonitrile proceeds via a stabilized vinyl cation[13] such as **14**. This gives the mixed anhydride **16** (via enol **15**), which rapidly reacts further to yield the observed acid products, as shown in Scheme II.

Protonation to give vinyl cation **14** is expected on the basis of the electron-donating ability of tosylates,[9] as in **7**, analogous to the known[13] protonation of alkynyl ethers, thioethers, and ynamines. Rapid reaction with water results in **15**, followed by tautomerism to give the mixed anhydride **16**. Mixed carboxylic–sulfonic anhydrides are known[14] to rapidly hydrolyze to their respective acids.

The exact mechanism of acid additions in CH_2Cl_2 is much more obscure and complex. There is little doubt that despite the mild reaction conditions (room temperature or below) as well as the relatively nonpolar solvent, CH_2Cl_2, vinyl cations (or ion pairs) of some sort are involved. What is somewhat surprising is the complete stereospecificity of the reaction and formation of a single product via syn addition. Two explanations may be offered and most likely

(10) Kutscheroff, M. G. *C. Ber. Dtsch. Chem. Ges.* **1881**, *14*, 1532, 1540; **1884**, *17*, 13. Fittig, R.; Schrohe, A. *Ibid.* **1875**, *8*, 367.
(11) Jacobs, T. C.; Searles, S. *J. Am. Chem. Soc.*, **1944**, *66*, 686.
(12) Hogeveen, H.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 410 and references therein.
(13) For a review, see: Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic: New York, 1979.
(14) Effenberger, F.; Epple, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 299.

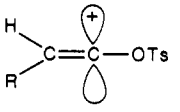
account for this observation. First, CH_2Cl_2 is probably insufficiently polar to properly solvate and dissociate either the starting acid or the resulting vinyl cation ion pair. A poorly solvated tight ion pair, **17**, would ipso facto collapse in a syn manner, resulting in the observed syn-addition products. Predominant (although seldom exclusive) syn



17

addition of strong acids to alkynes in nonpolar solvents via vinyl cation ion pairs is well precedented.[15]

Secondly, should a free vinyl cation **18**, which is rather unlikely, be involved, such linear but dissymetrically substituted vinyl cations possess diastereotopic sides (or faces) that ipso facto capture nucleophiles or solvent differentially from the two sides. Particularly in the case



18

of large substituents, such as *tert*-butyl and *sec*-butyl, attack of the nucleophile (counterion of the acid) from the less hindered side (with the H substituent), i.e. syn attack, should be greatly favored over the anti addition where the nucleophile would be forced to approach in the same plane as the bulky substituent.

In actuality, a combination of these two factors is most likely, and together they account for the complete stereospecificity observed. The bulk of the reaction most likely proceeds through tight ion pairs favoring syn addition and a small amount of reaction might proceed through "free" but diastereotopic vinyl cations that preferentially capture nucleophiles from the less hindered side also resulting in net syn addition.

Conclusion

A wide variety of proton acids (HCl, $ArSO_3H$, CF_3SO_3H, and CF_3CO_2H) readily add to alkynyl tosylates, under very mild conditions, via regio- and stereospecific syn addition, to give previously unknown vinyl 1,1-(bis esters) and related compounds in excellent yields. Vinyl cation tight ion pairs are the most likely intermediates. NMR spectral data and X-ray crystallography unambigiously establish product stereochemistry. Likewise, acid-catalyzed hydration results in the expected acid products also via vinyl cation intermediates.

Experimental Section

General Methods. Melting points (uncorrected) were obtained with a Mel-Temp capillary melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer. NMR spectra were recorded on either a Varian EM-390 or XL 300 spectrometer. Chemical shifts (^1H, ^{13}C) are reported relative to internal tetramethylsilane. ^{19}F NMR shifts (ppm) are reported relative to internal $CFCl_3$.

Materials. All commercial solvents and acids were reagent grade and used without further purification. The synthesis of the starting *tert*-butylalkynyl and *sec*-butylalkynyl tosylates and *tert*-butylalkynyl mesylate have been previously described.[3] Silica gel (Davisil) was not activated prior to use.

3,3-Dimethyl-1-chloro-1-(tosyloxy)-1-butene (2a). Alknyl tosylate **1a** (0.4 g, 1.6 mmol) was dissolved in 20 mL of dry CH_2Cl_2, degassed with argon, and cooled to −20 °C. HCl gas was bubbled slowly through the solution for approximately 5 min followed by argon to remove excess acid. Removal of the solvent gave a light yellow oil; the IR spectrum showed that no triple bond remained. Column chromatography (silica gel, CH_2Cl_2) and rotary evaporation gave 0.45 g (>99%) of **2a** as a pale yellow solid: mp 58.0–58.5 °C; IR (neat) 3050, 2960, 1640, 1595, 1380, 1260, 1190, 1175, 1005, 850, 810, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, 2 H), 7.35 (d, 2 H), 5.30 (s, 1 H), 2.40 (s, 3 H), 1.15 (s, 9 H); ^{13}C NMR (300 mHz, $CDCl_3$) δ 145.5, 133.6, 130.9, 130.5, 129.6, 128.4, 33.5, 29.9, 21.7. Anal. Calcd for $C_{13}H_{17}O_3SCl$: C, 54.07; H, 5.94; S, 11.10; Cl, 12.28. Found: C, 54.33; H, 5.99; S, 11.64; Cl, 13.14.

3-Methyl-1-chloro-1-(tosyloxy)-1-pentene (2b). The reaction was performed as above with 0.28 g (1.1 mmol) of *sec*-butylalkynyl tosylate **1b**. Chromatography and removal of solvent gave 0.30 g (>99%) of **2b** as a pale yellow oil: IR (neat) 3040, 2960, 1645, 1595, 1380, 1190, 1175, 1000, 855, 810, 700, 670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, 2 H), 7.35 (d, 2 H), 5.20 (d, J = 11 Hz, 1 H), 2.45 (s + m, 4 H), 1.3 (m, 2 H), 0.95 (d, 3 H), 0.80 (t, 3 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 145.7, 132.9, 131.0, 129.7, 129.6, 128.3, 34.0, 29.5, 21.7, 19.6, 11.6. Anal. Calcd for $C_{13}H_{17}O_3SCl$: C, 54.07; H, 5.94; S, 11.10; Cl, 12.28. Found: C, 53.37; H, 5.84; S, 11.14; Cl, 14.10.

General Procedure for Acid Addition to Alkynyl Tosylates. 3,3-Dimethyl-1,1-bis(tosyloxy)-1-butene (3a). To a solution of **1a** (0.50 g, 2.0 mmol) in CH_2Cl_2 (20 mL) was added 0.40 g (2.1 mmol) of *p*-TsOH·H_2O. The suspension was stirred vigorously overnight. An IR spectrum of the crude CH_2Cl_2 solution showed that none of the 2270-cm^{-1} band of the starting material remained. The CH_2Cl_2 solution was decanted from the remaining *p*-TsOH·H_2O and reduced in volume to approximately 5 mL. The crude ditosylate was chromatographed on a silica gel column (10 cm × 1 cm) with CH_2Cl_2 to remove traces of acid. Removal of solvent gave 0.85 g (>99%) of 3,3-dimethyl-1,1-bis(tosyloxy)-1-butene (**3a**) as an oil, which solidified on standing. Recrystallization from CH_2Cl_2/hexanes gave colorless crystals: mp 65–66 °C; IR (neat) 3050, 2960, 1680, 1595, 1380, 1190, 1175, 1060, 975, 810, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, 2 H), 7.45 (d, 2 H), 7.30 (d, 2 H), 7.20 (d, 2 H), 4.85 (s, 1 H), 2.45 (s, 3 H), 2.40 (s, 3 H), 1.10 (s, 9 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 145.6, 145.5, 139.5, 133.3, 131.0, 129.5, 129.4, 128.4, 121.4, 31.2, 29.8, 21.8, 21.7. Anal. Calcd for $C_{20}H_{24}O_6S_2$: C, 56.56; H, 5.70; S, 15.11. Found: C, 56.74; H, 5.70; S, 15.34.

3-Methyl-1,1-bis(tosyloxy)-1-pentene (3b). The ditosylate was made by the general procedure from 0.50 g of **1b** and 0.40 g of *p*-TsOH·H_2O. The yield after chromatography (silica gel, CH_2Cl_2) was 0.85 g (>99%) of **3b** as a colorless oil: IR (neat) 3050, 2980, 1685, 1595, 1380, 1190, 1175, 1060, 810, 740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, 2 H), 7.55 (d, 2 H), 7.30 (d, 2 H), 7.25 (d, 2 H), 4.85 (d, J = 11 Hz, 1 H), 2.45 (s, 3 H), 2.40 (s, 3 H), 2.30 (m, 1 H), 1.25 (m, 2 H), 0.90 (d, 3 H), 0.80 (t, 3 H); ^{13}C (300 MHz, $CDCl_3$) δ 145.6, 140.3, 132.7, 131.5, 129.7, 129.5, 129.4, 128.2, 128.1, 118.2, 32.4, 29.5, 21.6, 19.7, 11.5.

3,3-Dimethyl-1-[[(*m*-nitrophenyl)sulfonyl]oxy]-1-(tosyloxy)-1-butene (4a). The compound **4a** was obtained by the general procedure from 0.4 g (1.6 mmol) of **1a** and 0.4 g (2.0 mmol) of *m*-nitrobenzenesulfonic acid. The yield was 0.75 g (>99%) of **4a** as a white solid: mp 93.5–94.0 °C; IR (Nujol) 3095, 1670, 1605, 1590, 1540, 1385, 1350, 1190, 1050, 810, 680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.50–7.25 (m, 8 H), 5.10 (s, 1 H), 2.50 (s, 3 H), 1.10 (s, 9 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 147.8, 146.2, 139.2, 136.6, 133.8, 133.0, 130.4, 129.7, 128.6, 128.4, 123.5, 122.8, 31.5, 29.9, 21.8. Anal. Calcd for $C_{19}H_{21}O_8S_2N$: C, 50.10; H, 4.65; S, 14.08; N, 3.08. Found: C, 50.44; H, 4.74; S, 14.45; N, 3.14.

3-Methyl-1-[[(*m*-nitrophenyl)sulfonyl]oxy]-1-(tosyloxy)-1-pentene (4b). The compound **4b** was obtained from 0.4 g (1.6 mmol) of **1b** and 0.4 g (2.0 mmol) of *m*-nitrobenzenesulfonic acid. The yield was 0.75 g (>99%) of **4b** as a white solid: mp 68.5–69.0 °C; IR (neat) 3080, 2960, 1685, 1600, 1535, 1385, 1350, 1190, 1050, 810, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.50–7.25 (m, 8 H), 5.05 (d, J = 11 Hz, 1 H), 2.45 (s, 3 H), 2.20 (m, 1 H), 1.30 (m, 2 H), 0.95 (d, 3 H), 0.85 (t, 3 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 147.8, 146.2, 140.0, 137.0, 133.8, 132.3, 130.5, 129.8, 128.7, 128.1, 123.5, 119.6, 32.6, 29.6, 21.8, 19.8, 11.6. Anal. Calcd for $C_{19}H_{21}O_8S_2N$: C, 50.10; H, 4.65; S, 14.08; N, 3.08. Found: C, 50.38; H, 4.77; S, 14.32; N, 3.07.

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3,3-Dimethyl-1-[[(trifluoromethyl)sulfonyl]oxy]-1-(tosyloxy)-1-butene (5a). Alkynyl tosylate **1a** (0.2 g, 0.8 mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled to 0–5 °C. Triflic acid (0.1 mL, 1.1 mmol) was added over ~5 min, and the reaction was stirred for another 5 min. The reaction was quickly purified by the standard procedure and gave 0.2 g (60%) of **5a** as a colorless oil. The oil darkened on standing and so all spectra were taken within the hour. **5a**: IR (neat) 3050, 2960, 1690, 1595, 1400, 1200, 810, 730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, 2 H), 7.40 (d, 2 H), 5.25 (s, 1 H), 2.45 (s, 3 H), 1.20 (s, 9 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 146.5, 139.1, 132.5, 130.0, 128.5, 122.7, 188.1 (q, J_{C-F} = 4.25 ppm), 31.8, 29.6, 21.8.

3-Methyl-1-[[(trifluoromethyl)sulfonyl]oxy]-1-(tosyloxy)-1-pentene (5b). This compound was prepared according to the procedure for **5a** with 0.2 g (0.8 mmol) of **1b** and 0.1 mL (1.1 mmol) of triflic acid. The yield of **5b** was 0.13 g (40%) as a light tan oil: IR (neat) 3050, 2960, 1685, 1595, 1400, 1210, 810, 790, 680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, 2 H), 7.40 (d, 2 H), 5.10 (d, J = 11 Hz, 1 H), 2.40 (s, 3 H), 2.30 (m, 1 H), 1.30 (m, 2 H), 0.95 (d, 3 H), 0.85 (t, 3 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 146.6, 139.8, 132.0, 130.0, 128.4, 119.7, 32.8, 29.5, 21.8, 19.6, 11.4.

3,3-Dimethyl-1-(trifluoroacetoxy)-1-(tosyloxy)-1-butene (6a). Alkynyl tosylate **1a** (0.4 g, 1.6 mmol) and trifluoroacetic acid (0.2 g, 1.8 mmol) were stirred in 25 mL of CH_2Cl_2 for 1 h and then purified by the general procedure. The yield of **6a** was 0.5 g (85%) as a light yellow oil: IR (neat) 3050, 2960, 1810, 1690, 1595, 1390, 1220, 1175, 1115, 1065, 810, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, 2 H), 7.40 (d, 2 H), 5.10 (s, 1 H), 2.45 (s, 3 H), 1.20 (s, 9 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 146.2, 138.5, 132.9, 129.9, 128.1, 119.6, 114.0 (q, J_{C-F} = 4 ppm) 31.4, 29.9, 21.7.

3-Methyl-1-(trifluoroacetoxy)-1-(tosyloxy)-1-pentene (6b). This adduct was prepared as above from 0.4 g (1.6 mmol) of **1b** and 0.2 g (1.8 mmol) trifluoroacetic acid. The yield was 0.30 g (50%) of **6b** as a light yellow oil: IR (neat) 3050, 2960, 1810, 1695, 1595, 1390, 1220, 1175, 810, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, 2 H), 7.40 (d, 2 H), 5.00 (d, J = 11 Hz, 1 H), 2.45 (s, 3 H), 2.30 (m, 1 H), 1.30 (m, 2 H), 0.95 (d, 3 H), 0.85 (t, 3 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 146.3, 139.4, 132.2, 129.9, 128.2, 116.7, 113.8 (q, J_{C-F} = 3.8 ppm), 32.3, 29.5, 21.6, 19.7, 11.5.

Preparation of Isomeric Diesters 11a and 11b. Compound **11b** was prepared from 0.1 g (0.4 mmol) of alkynyl mesylate **10** and 0.2 g (1 mmol) $TsOH{\cdot}H_2O$ by stirring overnight in 20 mL of CH_2Cl_2. The yield was 0.18 g (90%). Compound **11a** was prepared from **1a** (0.1 g, 0.4 mmol) and 0.1 g (1 mmol) of 98% MsOH by stirring for 1 h. The yield was 0.2 g (99%+).

Spectral data for **11b**: IR (neat) 3040, 2960, 1680, 1595, 1370, 1180, 1060, 730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, 2 H), 7.25 (d, 2 H), 4.60 (s, 1 H), 3.20 (s, 3 H), 2.50 (s, 3 H), 1.50 (s, 9 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 146.3, 139.5, 130.7, 130.0, 128.8, 121.5, 41.0, 31.2, 29.9, 21.8.

Spectral data for **11a**: IR (neat) 3020, 2970, 1680, 1590, 1370, 1180, 1060, 730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, 2 H), 7.40 (d, 2 H), 5.20 (s, 1 H), 2.80 (s, 3 H), 2.50 (s, 3 H), 1.15 (s, 9 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 146.0, 138.9, 133.1, 129.8, 128.5, 121.5, 38.1, 31.4, 29.9, 21.8.

General Procedure for Hydration of Alkynyl Esters. Formation of *tert*-Butylacetic Acid (12a). In a 25-mL flask were placed 5 mL of distilled H_2O, 5 mL of CH_3CN and 0.20 g (0.8 mmol) of *tert*-butylalkynyl tosylate **1a**. One drop of concentrated (~30%) HCl was added, and the heterogeneous reaction mixture was refluxed for 24 h at which time the solution was homogeneous. The reaction was allowed to cool and then the CH_3CN was removed on a rotary evaporator. The residue was partitioned between CH_2Cl_2 and H_2O. After drying of the CH_2Cl_2 layer over Na_2SO_4, filtration, and removal of solvent, an oil was obtained, which on cooling gave **12a** as a tan solid (83 mg, 90%). On drying of the H_2O layer in the air, a quantitative yield of $TsOH{\cdot}H_2O$ was obtained. The IR and ^1H NMR spectra of all materials matched the literature data.[16]

Formation of 3-Methylvaleric Acid (12b). The reaction was performed as above with *sec*-butylalkynyl tosylate **1b** (0.20 g, 0.8 mmol). The yield of slightly impure 3-methylvaleric acid was 80 mg (87%). A quantitative yield of $TsOH{\cdot}H_2O$ was obtained after evaporation of H_2O layer. The IR and ^1H NMR spectra agreed with literature.[16]

X-ray Crystallography of 3,3-Dimethyl-1-chloro-1-(tosyloxy)-1-butene (2a). Unit cell determination and data collection were performed on a Syntex P1 diffractometer. The unit cell was determined with 15 centered reflections with $16° < 2\theta < 29°$. Details of the data collection are listed in Table II. The structure was solved with standard direct methods by using the UCLA Crystallographic Package. Programs used include CARESS (Robert W. Broach, Chemistry Division, Argonne National Laboratory) (Program CARESS incorporates features of PROFILE (Blessing, R. G.; Coppend, P.; Becker, P. *J. Appl. Crystallogr.* **1972**, *7*, 488–492)), NORMAL, EXFFT, and SEARCH (all from the MULTAN 80 package, Peter Main, Department of Physics, University of York, York England), ORFLS, (ORNL-TM-305), ORFE (ORNL-TM-306), and ORTEP (ORNL-TM-5138)). The least-squares refinement program, ORFLS, was modified to allow the refinement of the coefficients of a scale function that was a quadratic function of exposure time, as described by Ibers (Ibers, J. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 1667–1668). Hydrogen atoms were generally placed in assigned positions. Non-hydrogen atoms were refined with anisotropic thermal parameters. Final refinement gave an R value of 5.7 (R_w = 5.5).

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Registry No. **1a**, 90893-24-6; **1b**, 110745-73-8; **2a**, 110745-74-9; **2b**, 110745-75-0; **3a**, 110745-76-1; **3b**, 110745-77-2; **4a**, 110745-78-3; **4b**, 110745-79-4; **5a**, 110745-80-7; **5b**, 110745-81-8; **6a**, 110745-82-9; **6b**, 110745-83-0; **10**, 105639-61-0; **11a**, 110745-85-2; **11b**, 110745-84-1; **12a**, 1070-83-3; **12b**, 105-43-1; MsOH, 75-75-2; TsOH, 104-15-4; *m*-$O_2NC_6H_4SO_3H$, 98-47-5; HCl, 7647-01-0; F_3CSO_3H, 1493-13-6; F_3CCO_2H, 76-05-1.

Supplementary Material Available: Details of X-ray data and ORTEP view of **2a** (6 pages); observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

(16) Pouchert, C. J. *The Aldrich Library of Infrared Spectra*; 1981; Vol. III, *tert*-butylacetic acid 287G; 3-methylvaleric acid 288B. Pouchert, C. J. *The Aldrich Library of NMR Spectra*, 2nd Ed.; 1983; *tert*-butylacetic acid *1*, 426A, 3-methylvaleric acid *1*, 426B.