For $^-O_2N=C(R_1)(R_2)$ the reactivity series is the following: R_1, $R_2 = H(NO_2)$, NO_2; R_1, $R_2 = o,o'$-biphenylenyl ($\sigma^* \sim 1.4$) < R_1, $R_2 = Ph$, H ($\sum\sigma^* = 1.09$) < $R_1 = R_2 = H$ ($\sum\sigma^* = 0.98$) > R_1, $R_2 = Ph$, CH_3 ($\sum\sigma^* = 0.60$) > R_1, $R_2 = H$, CH_3 ($\sum\sigma^* = 0.49$) > $R_1 = R_2 = CH_3$ ($\sum\sigma^* = 0$). The decrease in reactivity of the phenone enolate anions more basic than $PhC(O^-)=CPh_2$ ($\sum\sigma^* \le 1.20$) gives $\rho^* = 1.5$ ($r = 0.996$) while the nitronates with $\sum\sigma^*_{R_1,R_2} \le 0.98$ give $\rho^* = 1.56$ ($r = 0.997$),[10]

The factors controlling the inverted reactivity order appear to be the exoergicity of the reaction and the nucleophilic character of the alkyl free radical. For weakly basic anions that fail to react with $Me_3C\cdot$, the reaction is apparently too endothermic to occur readily.[11] As the exoergicity to the reaction increases, the reactivity of the nucleophile at first increases and then decreases as the nucleophilic character of the *tert*-butyl radical becomes a more obvious factor in determining the energy of the transition state.[12] The reactivity of phenone but not of pinacolone or ester enolates may be connected with the stability of the resulting radical anions ($Ph\dot{C}(O^-)C(Ph)_2CMe_3 > Me_3C\dot{C}(O^-)C(Ph)_2CMe_3$, $EtO\dot{C}(O^-)C(Ph)_2CMe_3$).

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(9) Values of $\Delta G°$ were calculated by the thermochemical cycle of Tolbert[5] with the group additivity rules of Benson, et al. (Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Revs.* **1969**, *69*, 279) and pK$_a$'s in Me$_2$SO given by Bordwell, et al. (Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Drucker, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006).

(10) A similar decrease in reactivity from $H_2C=NO_2^-$ to $Me_2C=NO_2^-$ toward CH_3· in H_2O ($\rho^* = 1.8$) has been noted by Veltwisch and Asmus.[6]

(11) Reaction of anions with the less nucleophilic Me_2CNO_2 leads to the more stable RNO_2^-·. Thus, $(EtO)_2PO^-$ or $HC(CO_2Et)_2^-$, which show no reactivity toward $Me_3C\cdot$, are readily trapped by Me_2CNO_2: Russell, G. A.; Ros, F.; Mudryk, B. *J. Am. Chem. Soc.* **1980**, *102*, 7601.

(12) If $\Delta G^{\ddagger}$ is determined by the transfer of an electron from the radical SOMO to the anion LUMO to form π^* before significant σ-bond formation occurs, a decrease or increase in the LUMO energy from some optimum value could result in a rate decrease when the SOMO and π^* energy levels are held constant.

Alkynyl Sulfonate Esters. Preparation and Characterization of Acetylenic Tosylates, RC≡COTs

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Acetylenes have intrigued chemists since their discovery in the 19th century. Besides simple acetylenes numerous functionalized alkynes are known and play an important role in mechanistic as well as synthetic organic chemistry.[1] Despite the diversity of functionalized acetylenes alkynyl sulfonate esters are to date unknown. In this paper we wish to disclose our preliminary results for the simple, general preparation of alkynyl tosylates and their spectral and chemical characterization.

The synthesis of three representative alkynyl tosylates is outlined in Scheme I. Treatment of commercial[2] iodosobenzene diacetate (1) with toluenesulfonic acid monohydrate (2) in acetonitrile, according to Koser and Wettach,[3] affords phenylhydroxy(tosyloxy)iodine (3) in greater than 90% yield. The structure of this unusual hypervalent organoiodine 3 is securely established by
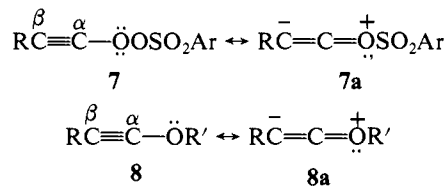
Scheme I
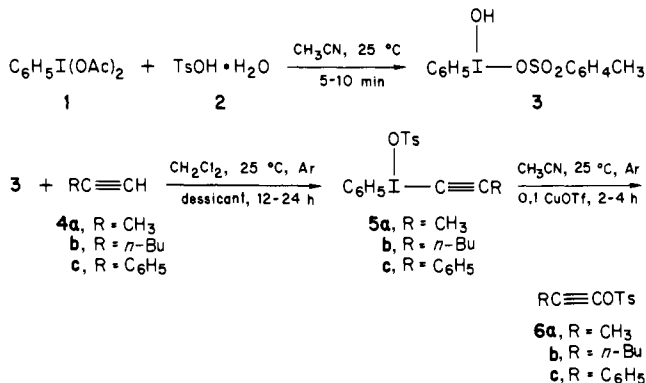
Scheme II
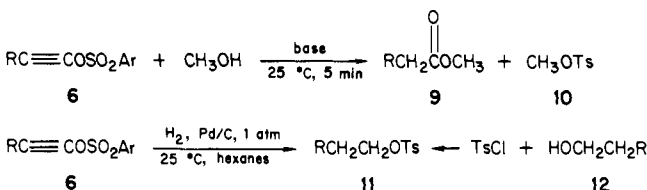
X-ray data.[4] Interaction of 3 with terminal acetylenes 4 by procedures analogous to those of Koser et al.[5] gives phenyl(alkynyl)iodonium tosylates (5) in 20–60% yields, as crystalline solids.[6] Stirring of iodonium tosylates 5 with 0.1 equiv of copper(I) triflate[7] in acetonitrile gives alkynyl tosylates 6 in 50–60% isolated yields on a 1 mM scale. Pure alkynyl tosylates 6a and 6b are *stable*, nearly colorless, pale yellow oils. Alkynyl tosylate 6c is reasonably stable in solution but decomposes when neat in a few hours.

Structural assignments for these new, novel alkynyl tosylates[8] 6 were made by spectral and chemical means. The spectral data are summarized in Table I.

Chemical ionization mass spectrum, using CH_4 as the ionizing gas, affords appropriate molecular ions, ion clusters, and fragmentation patterns. In the infrared there are very characteristic strong absorptions at 2280 cm^{-1} for the triple bond and three strong absorptions centered around 1395 and 1185 cm^{-1} for the antisymmetric and symmetric SO_2 and at 685 cm^{-1} for the C–O–S absorptions of the tosylate functionality. The proton NMR are consistent with the proposed structures, including the characteristic tosylate pattern. Particularly noteworthy are the acetylenic carbon signals in the ^{13}C NMR. Whereas the α-C's are in the normal acetylenic region the β-C's are uniformly shifted upfield by nearly 30 ppm. This, at first surprising, result is readily rationalized by the contribution of the resonance hybrid 7a in analogy to alk-

oxyalkynes (8) where the β-C for $EtC≡COEt$ is at 36 ppm.[9] Such a resonance contribution by 7a is in accord with the known[10]

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(6) All iodonium tosylates 5 had spectral data (IR and NMR) in accord with their structures: 5a, mp 121–127 °C dec, 2190 cm^{-1} (C≡C); 5b, mp 81–84 °C dec, 2180 cm^{-1} (C≡C), 5c, mp 118–124 °C dec, 2155 cm^{-1} (C≡C).

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(8) Tosylates 6a and 6b gave satisfactory C, H, and S analyses, while 6c was too unstable for analyses.

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Table I. Spectral Data for Alkynyl Tosylates **6**

$$H_3C-\overset{5}{\underset{4}{}}\!\!\!\!\!\! \langle \overset{3\ 2}{\underset{}{}} \rangle \overset{1}{} SO_2OC\overset{6\ 7}{\equiv}CR$$

compd	R	IR,[a] cm^{-1}	mass spectrum,[b] m/e (%)	^{1}H NMR,[c] δ	^{13}C NMR,[d] δ
6a	CH_3	2280 (C≡C), 1595 (Ar), 1395 (SO$_2$), 1215 (d), 1185 (d, SO$_2$), 810 (para disub Ar), 685 (≡COS)	251 (2.2, M + 41), 239 (3.0, M + 29), 225 (1.8, M + 15), 211 (100, M + 1), 185 (27), 157 (72), 155 (31), 139 (35)	7.71 (d, J = 8 Hz, 2 H, H$_2$), 7.24 (d, J = 8 Hz, 2 H, H$_3$), 2.35 (s, 3 H, H$_5$), 1.59 (s, 3 H, H$_8$)	148.2 (C$_1$), 130.9, 130.6 (C$_4$), 129.7, 77.9 (C$_6$), 44.1 (C$_7$), 22.0 (C$_5$), 1.6 (C$_8$)
6b	n-C$_4$H$_9$	2275 (C≡C), 1594 (Ar), 1395 (SO$_2$), 1185 (d, SO$_2$), 814 (para disub Ar), 690 (≡COS)	294 (3.3, M + 42), 281 (2.1, M + 29), 267 (8.3, M + 15), 253 (11.2, M + 1), 251 (11.5, M − 1), 155 (100), 139 (61), 97 (21.3, C$_6$H$_9$O), 91 (49), 85 (72)	7.87 (d, J = 8.2 Hz, 2 H, H$_2$), 7.44 (d, J = 8.7 Hz, 2 H, H$_3$), 2.48 (s, 3 H, H$_5$), 2.10 (t, J = 6.9 Hz, 2 H, H$_8$), 1.42-1.21 (m, 4 H, H$_{9,10}$), 0.85 (t, J = 7.3 Hz, 3 H, H$_{11}$)	148.2 (C$_1$), 130.8, 130.6 (C$_4$), 129.8, 79.2 (C$_6$), 48.4 (C$_7$), 31.1, 22.1, 22.0, 16.9, 13.7
6c	C_6H_5	2260 (C≡C), 1596 (Ar), 1390 (d, SO$_2$), 1185 (d, SO$_2$), 810 (para disub Ar), 685 (≡COS)		7.96 (d, J = 8.5 Hz, 2 H, H$_2$), 7.46 (d, J = 8.1 Hz, 2 H, H$_3$), 7.31 (s, 5 H, H$_{9-13}$), 2.48 (s, 3 H, H$_5$)	148.3 (C$_1$), 131.9, 130.4 (2 C), 129.4, 128.6 (2 C), 120.8 (C$_8$), 87.2 (C$_6$), 48.2 (C$_7$), 21.7 (C$_5$)

^{a} Neat with **6a-c** as Nujol mull. ^{b} Chemical ionization, CH$_4$ ionizing gas. ^{c} All spectra run in CD$_2$Cl$_2$, **6a** at 90 MHz, **6b** at 300 MHz, **6c** at 80 MHz and at −50 °C. ^{d} All spectra run in CD$_2$Cl$_2$ at 75 MHz, **6c** at −57 °C.

Scheme III
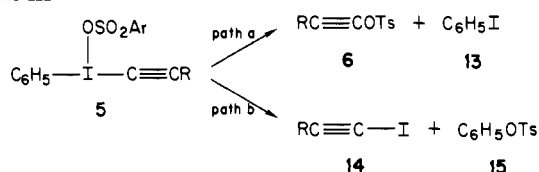
electronic effects of sulfonates and in particular a σ_p = +0.29 and σ_I = +0.54 but a σ_R = −0.21 for the tosylate group.

Further proof for the structures of **6** comes from methanolyses and hydrogenation as shown in Scheme II. Reaction with basic methanol gives saturated esters **9**, presumably via ketenes RCH=C=O or ketene equivalents RC≡C—O$^-$, along with methyl tosylate **10**, identical in all respects with authentic materials prepared by standard procedures. Likewise hydrogenation affords saturated tosylates **11** identical with authentic samples prepared, from the appropriate alcohols **12** and tosyl chloride, by standard procedures. Hence there is no doubt about the structure of these alkynyl sulfonate esters.

Decomposition of **5** to **6** deserves further comment. As Scheme III indicates there are two modes of decomposition for the hypervalent[11] 10-I-3 species **5**. Path a gives the desired esters **6** along with iodobenzene **13**, whereas path b results in iodoalkynes **14** along with phenyl tosylate **15**. In a formalistic sense both pathways represent ligand–ligand couplings in a hypervalent nonmetallic species,[11] analogous to the well-known reductive eliminations in organometallic chemistry. It is difficult to predict a priori which pathway should predominate. Preliminary studies indicate that thermolyses[12] or photolyses[12] of **5c** favors path b whereas simple stirring with CuOTf favors the desired path a. We do not understand this dichotomy of behavior and the mechanism of decomposition of **5** is under active investigation.

In summary, we have developed a mild, simple, general means of synthesizing novel alkynyl tosylates from readily available precursors via hypervalent iodine intermediates. Alkyl-substituted acetylenic sulfonates **6a** and **6b** are stable, nearly colorless oils, with characteristic, consistent spectral properties. The full scope of this methodology along with the mechanism involved are under active investigation as are the reactions and chemistry of these

unique alkynyl sulfonates and will be the subject of future reports.

Thermodynamic and Kinetic Properties of the Metaphosphate Anion, PO$_3^-$, in the Gas Phase

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Whereas PO$_3^-$ is proposed to be a reactive intermediate in solution, we report here that PO$_3^-$ is thermodynamically stable and undergoes no chemical reactions in the gas phase.

The metaphosphate anion, PO$_3^-$, was first suggested as an intermediate in the aqueous hydrolysis of phosphate esters some 30 years ago,[3] and this possibility has been investigated vigorously ever since.[4] The metaphosphate anion has proved to be elusive, with, even today, only indirect evidence for its presence in solution, and a plausible explanation is that it reacts too fast to be observed.[5] Recent studies provide evidence for "free" PO$_3^-$ in some systems[6] but not in others.[7]

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(11) For an excellent review on hypervalent nonmetallic species, see: Martin, J. C. *Science (Washington, D.C.)* **1983**, *221*, 509.

(12) Thermolyses were carried out in refluxing benzene and photolyses in chlorofom with a Hanovia lamp equipped with a Pyrex filter. The resulting products C$_6$H$_5$C≡CI and **15** were identified by comparison with authentic materials. C$_6$H$_5$C≡CI was made by reaction of C$_6$H$_5$C≡CLi with I$_2$.

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(2) Air Force Geophysics Scholar.

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