

Table I. Computed IR Spectrum of Methylene cyclopropene 1 and Deuterated Derivatives^{a,c}

C ₄ H ₄ (1)		1-1,3,4,4-d ₄		1-1,3-d ₂		1-4,4-d ₂		symmetry	description
freq	rel int	freq	rel int	freq	rel int	freq	rel int		
3502	0.01	2679	0.04	2678	0.04	3502	0.00	A ₁	sym C-H str, ring H's
3460	0.00	2550	0.02	2550	0.00	3460	0.00	B ₂	antisym C-H str, ring H's
3419	0.08	2547	0.04	3419	0.08	2548	0.06	B ₂	antisym C-H str, CH ₂
3337	0.02	2439	0.01	3337	0.02	2440	0.02	A ₁	sym C-H str, CH ₂
1960	1.00	1894	1.07	1923	1.10	1936	0.93	A ₁	sym ring deformation strongly coupled with C ₂ =C ₄ stretch
1741	0.20	1654	0.08	1657	0.06	1733	0.27	A ₁	C ₁ =C ₃ stretch coupled with C ₂ =C ₄ stretch
1599	0.03	1234	0.01	1598	0.03	1248	0.02	A ₁	CH ₂ scissoring
1258	0.07	1170	0.04	1232	0.03	1240	0.08	B ₂	b
1183	0.02	986	0.00	1090	0.01	1091	0.00	B ₂	b
1124	0.02	948	0.02	1022	0.03	1076	0.00	A ₁	sym ring H in-plane deformation coupled with sym ring deformation
967	0.02	778	0.02	833	0.02	861	0.02	B ₂	b
918	0.01	715	0.00	722	0.00	873	0.00	A ₁	see 1124
878	0.40	717	0.29	878	0.38	698	0.09	B ₁	methylene H out of plane
791	0.22	645	0.00	669	0.08	794	0.34	B ₁	ring H out of plane
493	0.07	422	0.10	434	0.09	474	0.09	B ₁	C ₂ =C ₄ out-of-plane bend
393	0.01	332	0.01	368	0.01	352	0.00	B ₂	b

^aFrequencies are in cm⁻¹, and intensities are given relative to the 1960-cm⁻¹ band of C₄H₄. ^bThese bands are a result of strong coupling of antisymmetric ring deformation, C₂=C₄ in-plane bend, ring H antisymmetric in-plane deformation, and CH₂ rock. ^cIn addition to the IR-active bands two A₂ Raman frequencies are computed at 588 and 1025 cm⁻¹ for 1 at 427 and 833 cm⁻¹ for the d₄, at 581 and 833 cm⁻¹ for the 1,3-d₂ and at 437 and 1024 cm⁻¹ for the 4,4-d₂ derivatives. They result from CH₂ torsion and antisymmetric ring H out of plane.

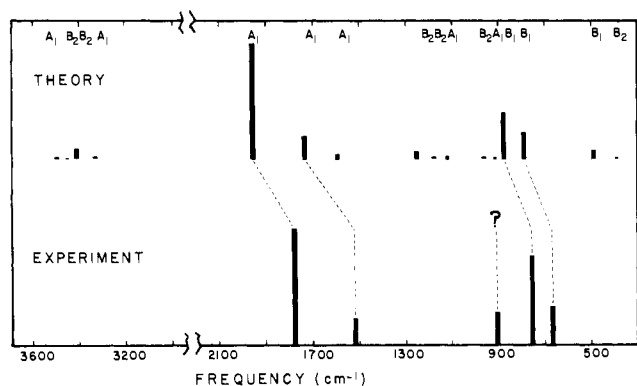


Figure 1. Comparison of the theoretical 6-31G* spectrum with the experimental spectrum of methylenecyclopropene reported by Billups.¹ Relative intensities are shown by bar heights.

carried out as previously described.⁴⁻⁸ Force constants were gotten from finite differences of analytically computed gradients. The dipole moment derivatives used in the intensity calculations were evaluated from internal coordinate displacements. In Table I these are given along with those for three yet unknown deuterated derivatives of 1. Also given are the individual symmetries of the bands and a description of the corresponding predominant motions as given by the eigenvectors of the GF matrix.

In Figure 1 the computed spectrum of 1 is compared with the experimental spectrum reported by Billups.¹ His spectrum contains many weak bands which he was unable to assign to methylenecyclopropene (in part due to impurities), and we have therefore plotted only the five bands which were attributed to 1. It is seen that the computed spectrum contains four intense bands while five relatively intense bands are found experimentally. There is good agreement for the two higher wave number bands. They are of A₁ symmetry and arise from strong coupling between the exo double bond stretch and ring deformation, in agreement with Billups' tentative assignment. However, at longer wavelengths we predict only two intense bands (B₁). These are due to the out-of-plane bending of the two types of hydrogens. We suggest these two correspond to the experimental 754- and 664-cm⁻¹ bands and that the experimental band at 904 cm⁻¹ is likely due to an impurity, perhaps isobutylene.¹³

Although the theoretical spectrum in Figure 1 is for isolated molecules at 0 K while the experimental spectrum was taken in

an argon matrix at 15 K, and although computed frequencies are all higher (as is usual) than the corresponding observed lines, the strong similarity in pattern of the two spectra does support Billups' and Staley's report of the first successful synthesis of methylenecyclopropene.

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An Inverted Reactivity Series in the Reaction of *tert*-Butyl Radical with Nucleophiles¹

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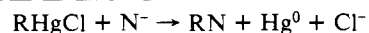
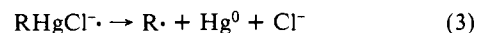
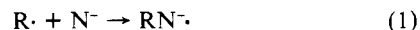
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Alkylmercury halides will participate in S_{RN}1 reactions with certain nucleophiles (Scheme I)² and undergo analogous chain

Scheme I



reactions with neutral radicalphiles such as pyridines,³ tetramethylphenylenediamine,³ 1,1-di-*p*-anisylethylene,⁴ or benzyl isocyanide.⁴

Table I lists anions that we found capable of undergoing a photostimulated reaction with *t*-BuHgCl. The yields in Table I were those observed for the reaction of equimolar amounts of the nucleophiles and *t*-BuHgCl in Me₂SO or HMPA at 35 °C when

(1) Electron Transfer Processes. 33. This work was supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) Russell, G. A.; Hershberger, J.; Owen, K. *J. Am. Chem. Soc.* **1979**, *101*, 1312; *J. Organomet. Chem.* **1982**, *225*, 43. The relative reactivities of alkylmercuric chlorides toward Me₂C=NO₂⁻ are PhCH₂ (4.70) > Me₂C (1.00) > Me₂CH (0.07) > *n*-C₆H₁₃ (<0.005). This suggests that reactions 2 and 3 of Scheme I may occur in a concerted fashion.

(3) Unpublished results with Deliang Guo.

(4) To yield with *t*-BuHgCl, Me₃CCH=C(*p*-OCH₃C₆H₄)₂, and PhCH₂NHCO₂Me₃ after hydrolysis.

(13) We have recently been informed by Professor Billups that the absorption at 904 cm⁻¹ is not due to methylenecyclopropene. This now brings the experimental spectrum into good agreement with the theoretical spectrum.

Table I. Reaction of *t*-BuHgCl with Nucleophiles^a

nucleophile ^b	time, h	prod (% yield) ^c	rel react ^d
NO ₂ ^{-e}	2	Me ₃ CNO ₂ (71)	0.38
(R ₁)(R ₂)C=NO ₂ ⁻			
R ₁ = R ₂ = CH ₃	2	Me ₃ CC(Me) ₂ NO ₂ (69)	1.00
R ₁ = CH ₃ ; R ₂ = H	2	Me ₃ CCH(Me)NO ₂ (74)	6.06
R ₁ = R ₂ = H	2	Me ₃ CCH ₂ NO ₂ (68)	35.00
R ₁ = H; R ₂ = Ph	2	Me ₃ CCH(Ph)NO ₂ (71)	0.97
R ₁ = CH ₃ ; R ₂ = Ph	2	Me ₃ CC(Me)(Ph)NO ₂ (67)	7.37
R ₁ , R ₂ = <i>o,o'</i> -biphenylenyl	2	9- <i>tert</i> -butyl-9-nitrofluorene (0)	<0.005
R ₁ = H; R ₂ = NO ₂	6	Me ₃ CCH(NO ₂) ₂ (0)	<0.005
R ₁ = R ₂ = NO ₂	6	Me ₃ CC(NO ₂) ₃ (0)	<0.005
phthalimide ^{-e}	5	<i>N</i> - <i>tert</i> -butylphthalimide (72)	0.32 ^f
N ₃ ^{-e}	8	Me ₃ CN ₃ (34)	
PhCHCN ⁻	5	Me ₃ CCH(Ph)CN (4), PhCH ₂ CMe ₃ (11)	<0.01
Ph ₂ CR ⁻			
R = CN	2	Me ₃ CC(Ph) ₂ CN (48), Ph ₂ C=C=NCMe ₃ (26)	6.50
R = Ph	2 ^g	Ph ₃ CCMe ₃ (39)	
		6- <i>tert</i> -butyl-3-benzhydrylidene-1,4-cyclohexadiene (21), <i>p</i> -Me ₃ CC ₆ H ₄ C(Ph) ₂ CMe ₃ (5)	
R = H	2 ^g	Ph ₂ CHCMe ₃ (36)	
R = CO ₂ Et	8	EtO ₂ CC(Ph) ₂ CMe ₃ (0)	
R = COCMe ₃	6	Me ₃ CCOC(Ph) ₂ CMe ₃ (6)	<0.005
fluorenyl ⁻	2 ^g	9- <i>tert</i> -butylfluorene (44)	
RC(CO ₂ Et) ₂ ⁻			
R = Ph	7	PhC(CO ₂ Et) ₂ CMe ₃ (43)	0.02 ^f
R = H	6	HC(CO ₂ Et) ₂ CMe ₃ (<2)	<0.005
R = CH ₃	6	MeC(CO ₂ Et) ₂ CMe ₃ (<2)	<0.005
Me ₂ CC(O ⁻)=CH ₂	8	Me ₃ CCOCH ₂ CMe ₃ (7)	
PhC(O ⁻)=CR ₁ R ₂			
R ₁ = R ₂ = H	6	PhCOCH ₂ CMe ₃ (54)	
R ₁ = R ₂ = CH ₃	5	PhCOC(Me) ₂ CMe ₃ (21)	0.03
R ₁ = H; R ₂ = CH ₃	4	PhCOCH(Me)CMe ₃ (34)	0.20
R ₁ = H; R ₂ = Ph	2	PhCOCH(Ph)CMe ₃ (63)	1.09
R ₁ = R ₂ = Ph	2	PhCOC(Ph) ₂ CMe ₃ (57)	2.18
R ₁ , R ₂ = <i>o,o'</i> -biphenylenyl	8	9- <i>tert</i> -butyl-9-benzoylfluorene (8)	0.011
R ₁ = H; R ₂ = PhCO	8	PhCOCH(COPh)CMe ₃ (2)	<0.005
R ₁ = Ph; R ₂ = PhCO	8	PhCOC(Ph)(COPh)CMe ₃ (3)	<0.005
R ₁ = H; R ₂ = CN	8	PhCOCH(CN)CMe ₃ (2)	<0.005
R ₁ = H; R ₂ = CO ₂ Et	8	PhCOCH(CO ₂ Et)CMe ₃ (2)	<0.005

^aReactions were performed in nitrogen-purged Me₂SO in the presence of equimolar amounts of 18-crown-6, with irradiation from a 275-W sunlamp positioned ca. 15 cm from the Pyrex reaction flask. ^bGenerated by the action of potassium *tert*-butoxide on the conjugate acid. ^cYields determined by ¹H NMR and GLC on a 1-mmol scale for reactions 0.1 M in RHgX ≈ N⁻. ^dBased upon a series of experiments in Me₂SO at different N⁻ and Me₂C=NO₂⁻ concentrations (0.05–0.2 M) with [*t*-BuHgCl] = 0.01 M. Yields of the two alkylation products were in the range 80–95%. ^eCommercially available potassium salts were used. ^fLimiting value at high [*t*-BuHgCl] (>0.3 M) with [N⁻] = [Me₂C=NO₂⁻] ≈ 0.1–0.3 M. Reactions were terminated after consumption of 3% of the RHgX. ^gHMPA solvent.

irradiated with a sunlamp. Negligible reaction occurred in the dark, and the photostimulated reactions were drastically retarded by 10 mol % (*t*-Bu)₂NO. Reaction of Me₃C[•] with Ph₃C⁻ in HMPA gave rise to products from α and para attack as expected for radical attack upon the carbanion.⁵ The anion of diphenylacetone in Me₂SO also gave rise to a mixture of products from attack at carbon and nitrogen.

In the presence of nucleophiles, complex formation or ligand exchange in RHgX must be considered. As an indication of these processes, we have studied the competition between nucleophiles (N⁻) and Me₂C=NO₂⁻ at a variety of N⁻/*t*-BuHgCl ratios.⁶ A change in relative reactivity would be expected if complex formation between N⁻ and RHgCl was important or if the radical trapping step (reaction 1) was reversible. On the basis of experiments of this type, we conclude that PhCOCH₂⁻ and Me₃CCOCH₂⁻ form *t*-BuHgCH₂COR which undergoes photochemical decomposition to yield the enolate alkylation product without attack of Me₃C[•] upon Me₂C=NO₂⁻. Phthalimide and diethyl phenylmalonate gave a constant reactivity relative to Me₂C=NO₂⁻ only when [Me₂CHgCl]/[N⁻] was >1. With these exceptions, the other anions of Table I for which a relative reactivity is reported gave excellent linear plots of (yield Me₃C—CMe₂NO₂)/(yield Me₃C—N) vs. [Me₂C=NO₂⁻]/[N⁻] with a

zero intercept and $r > 0.998$ over a wide variety of concentrations of N⁻, Me₂C=NO₂⁻, and Me₃CHgCl. The results indicate no general correlation between the ease of oxidation of the nucleophiles and their reactivity.⁷ This result, as well as the absence of dimers such as NCC(Ph)₂C(Ph)₂CN, exclude reactions involving conversion of N⁻ to N[•].

The factors that control reactivity in the attack of a radical upon an anion are not well-defined.⁸ Table I illustrates the surprising result that the rates of reactions yielding a radical anion of constant stability (e.g., RNO₂⁻, RC(O⁻)C₆H₅ can at first increase and then decrease as the basicity of the anion increases. The change in ΔG° for the trapping of a radical by a series of nucleophiles to yield a radical anion of constant stability can be approximated by $\Delta\Delta G^\circ = -1.4\Delta pK_a$.⁵ For the series of PhC(O⁻)=C(R₁)(R₂), we observe the following reactivity order: R₁, R₂ = H(Ph), COPh (pK_a ~ 9, $\sum\sigma^*_{R_1,R_2} = 2-3$, $\Delta G^\circ \sim 16$) < R₁, R₂ = *o,o'*-biphenylenyl (pK_a = 10.1, $\sigma^* \cong 1.4$, $\Delta G^\circ = 14.4$) < R₁ = R₂ = Ph ($\sum\sigma^* = 1.20$) > R₁, R₂ = Ph, H (pK_a = 21.5, $\sum\sigma^* = 1.09$, $\Delta G^\circ = -1.6$) > R₁, R₂ = Me, H (pK_a = 24.4, $\sum\sigma^* = 0.49$, $\Delta G^\circ = -6.4$) > R₁ = R₂ = Me (pK_a = 26.3, $\sum\sigma^* = 0$, $\Delta G^\circ = -8.6$).⁹

(7) Russell, G. A.; Moye, A.; Nagpal, K. *J. Am. Chem. Soc.* **1962**, *84*, 4154.

(8) Tolbert has reported that the more basic Ph₃C⁻ is more reactive than *p*-PhC₆H₄C(Ph)₂⁻ toward Me[•] even though the reaction with Ph₃C⁻ is less exoergic. The preferred position of substitution in aromatic S_{RN1} reactions has also been rationalized as attack at the more basic site: Tolbert, L. M.; Siddiqui, S. J. *Org. Chem.* **1984**, *49*, 1744. We concur with Tolbert that exoergicity is an incomplete measure of reactivity, but we conclude that correlations with basicity can also be ambiguous.

(5) Tolbert, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 3531, 6808.

(6) Me₂C=NO₂⁻ is attacked by the 5-hexenyl radical in Me₂SO at 40 °C with $k = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (Russell, G. A.; Guo, D. *Tetrahedron Lett.* **1984**, *25*, 5239) and by CH₃[•] in H₂O at room temperature with $k = 2.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (Veltsch, D.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1143).

For $^-O_2N=C(R_1)(R_2)$ the reactivity series is the following: $R_1, R_2 = \dot{H}(NO_2), NO_2$; $R_1, R_2 = o,o'$ -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 $PhC(O^-)=CPh_2$ ($\sum\sigma^* \leq 1.20$) gives $\rho^* = 1.5$ ($r = 0.996$) while the nitronates with $\sum\sigma^*_{R_1, R_2} \leq 0.98$ give $\rho^* = 1.56$ ($r = 0.997$).¹⁰

The factors controlling the inverted reactivity order appear to be the exoergic 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 exoergic 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 ($Ph\dot{C}(O^-)C(Ph)_2CMe_3 > Me_3C\dot{C}(O^-)C(Ph)_2CMe_3, EtOC(O^-)C(Ph)_2CMe_3$).

(9) Values of ΔG^\ddagger were calculated by the thermochemical cycle of Tolbert⁵ 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_2SO given by Bordwell, et al. (Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, 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 $CH_3\cdot$ 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 ΔG^\ddagger is determined by the transfer of an electron from the radical SOMO to the anion LUMO to form π^* of the radical anion 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, $RC\equiv COTs$

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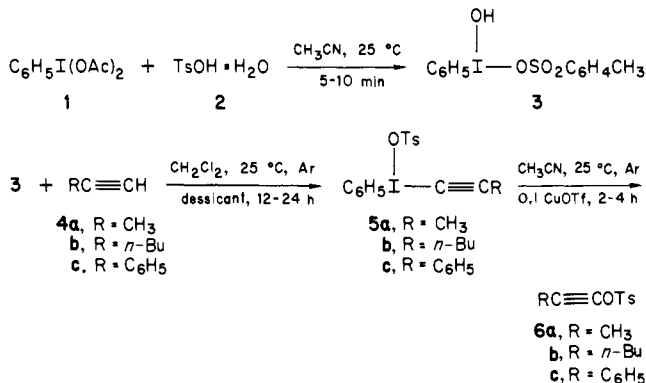
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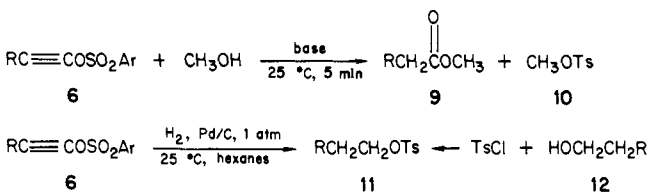
Acetylenes have intrigued chemists since their discovery in the 19th century. Besides simple acetylenes numerous functionalized alkynes are known and play an important role in mechanistic as well as synthetic organic chemistry.¹ Despite the diversity of functionalized acetylenes alkynyl sulfonate esters 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 commercial² 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



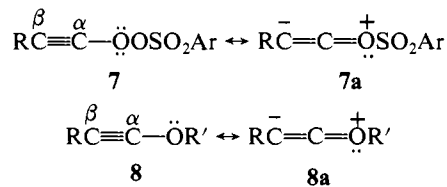
Scheme II



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) triflate⁷ 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 tosylates⁸ **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 anti-symmetric 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 $\text{EtC}\equiv\text{COEt}$ is at 36 ppm.⁹ Such a resonance contribution by **7a** is in accord with the known¹⁰

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

(5) Koser, G. F.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* 1981, 46, 4324.

(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} ($C\equiv C$); **5b**, mp 81–84 °C dec, 2180 cm^{-1} ($C\equiv C$); **5c**, mp 118–124 °C dec, 2155 cm^{-1} ($C\equiv C$).

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

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

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

(1) Reviews: "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S.; Ed.; Wiley-Interscience: London 1978; parts 1 and 2. Jäger, V.; Viehe, H. G. In "Methoden der Organischen Chemie (Houben-Weyl)"; Georg Thieme Verlag: Stuttgart, West Germany, 1977; 5/2a, Chapter 1, pp 1–916. Viehe, H. G. "Chemistry of Acetylenes"; Marcel Dekker: New York, 1969.

(2) Aldrich, or see: Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, pp 508–509.

(3) Koser, G. F.; Wettach, R.H. *J. Org. Chem.* 1977, 42, 1476. Rebrovic, L.; Koser, G. F. *Ibid.* 1984, 49, 4700.