°C; ^1H NMR 7.96 (2 H, dd, aromatic in positions 3 and 5); 7.01 (2 H, dd, aromatic in positions 2 and 6′), 6.77 (2 H, s, aromatic in positions 2′ and 6′), 3.59 (2 H, br s, exchangeable with D_2O, NH_2), 2.59 (3 H, s, $COCH_3$), 2.19 (6 H, s, 2 CH_3); IR ν_{NH_2} 3472 and 3370, $\nu_{C=O}$ 1670, $\nu_{=C-O}$ 1230. Alkaline extracts were acidified with concentrated HCl solution to give 3-(4-amino-3,5-dimethylphenyl)-4-hydroxyacetophenone (**6**), which was purified by crystallization from *i*-PrOH: mp 170°C; ^1H NMR 7.91 (2 H, m, aromatic in positions 2 and 4), 7.1 (3 H, m, aromatic in positions 5, 2′, and 6′), 3.92 (2 H, br s, exchangeable with D_2O, NH_2), 2.57 (3 H, s, $COCH_3$), 2.31 (6 H, s, 2 CH_3).

3,5-Dimethylphenylhydrazone of 3,5-Dimethyl-4-hydroxyacetophenone (7). A solution of (3,5-dimethylphenyl)hydrazine[10] (4.0 g) and 3,5-dimethyl-4-hydroxyacetophenone[6] (4.25 g) in EtOH (100 mL) was refluxed for 2 h in the presence of a trace of AcOH. The solvent was distilled, the solid residue dissolved in hot benzene (10 mL), and the resulting solution diluted with hexane (15 mL) to precipitate hydrazone **7**: mp 122 °C; 4.0 g (yield 52%).

Reaction of Hydrazone 7 with PPA. Hydrazone **7** (4.0 g) was added in portions with stirring to PPA (40 g) preheated at 80 °C in a oil bath. The reaction was exothermic. The temperature was then increased to 120 °C and kept there for 30 min. The mixture was poured into H_2O and the pH adjusted to 8 with 26% aqueous NH_3 solution. An oily product separated which was extracted with ether. The organic extract was dried (K_2CO_3) and the solvent removed to afford a residue which was dissolved in hot benzene. The resulting solution was diluted with an equal amount of hexane. 4-Acetyl-4′-amino-2,6,2′,6′-tetramethyldiphenyl ether (**9**) separated as yellow crystals: mp 121 °C (0.7 g); ^1H NMR 7.75 (2 H, s, aromatic in positions 3 and 5), 6.45 (2 H, s, aromatic in positions 3′ and 5′), 3.48 (2 H, br s, exchangeable with D_2O, NH_2), 2.58 (3 H, s, $COCH_3$), 2.12 and 2.0 (2 × 6 H, 2 s, 4 CH_3); IR ν_{NH_2} 3460 and 3360, $\nu_{C=O}$ 1670, $\nu_{=C-O}$ 1210.

2,6-Dimethylphenylhydrazone of 3,5-Dimethyl-4-hydroxybenzophenone (8). A solution of 3,5-dimethyl-4-hydroxybenzophenone[11] (12.2 g), (2,6-dimethylphenyl)hydrazine[7] (7.8 g), and AcOH (0.5 mL) in EtOH (50 mL) was refluxed for 4 h. The solvent was evaporated and the oily residue (18.6 g) chromatographed on a silica gel column (100 g, eluent $CHCl_3$). The first product eluted was hydrazone **8** as an orange viscous oil (9.2 g) which was used for the reaction with PPA without further purification due to its low stability.

Reaction of Hydrazone 8 with PPA. Hydrazone **8** (9.0 g) was added to PPA (100 g) preheated at 100 °C in a oil bath with stirring. After 1 h of additional heating, the mixture was poured into H_2O, and the crude gummy solid which separated was treated with diluted aqueous NH_3 solution and extracted with Et_2O. Removal of the solvent left an oily residue (1.9 g) which was chromatographed on a silica gel column (40 g, eluent $CHCl_3$). The main product of the reaction, 4-amino-4′-benzoyl-3,5,2′,6′-tetramethyldiphenyl ether (**10**), was collected after elution of a few minor fractions: mp 120 °C; ^1H NMR 7.8 (2 H, m, aromatic in position ortho of the C_6H_5CO group), 7.6 (5 H, m, aromatic in positions 3′ and 5′ and remaining aromatic of the C_6H_5CO group), 6.40 (2 H, s, aromatic in positions 2 and 6), 3.34 (2 H, br s, exchangeable with D_2O, NH_2), 2.16 and 2.13 (2 × 6 H, 2 s, 4 CH_3); IR ν_{NH_2} 3480 and 3350 $\nu_{C=O}$ 1650, $\nu_{=C-O}$ 1215.

2,6-Dimethylphenylhydrazone of 4-Hydroxybenzophenone (11). A mixture of 4-hydroxybenzophenone[9] (16.6 g) and (2,6-dimethylphenyl)hydrazine[7] (11.4 g) was heated at 120 °C on an oil bath for 1 h and then cooled and dissolved in benzene (5 mL). The solution was chromatographed through a silica gel column (250 g, eluent benzene) to remove tarry byproducts. Hydrazone **11** was rapidly eluted and purified by concentration of its benzene solution and dilution of the residue with cyclohexane: mp 141 °C; yield 6.0 g.

Reaction of Hydrazone 11 with PPA. Hydrazone **11** (6 g) was added to PPA (70 g) preheated at 80 °C with vigorous stirring. The reaction was slightly exothermic and was completed by heating the mixture at 120 °C for 1 h. The fluid mass was poured into H_2O to give a solid phosphoric acid salt, which was filtered and dissolved in a 10% NaOH solution. Impurities were removed by filtration, and the clear solution was acidified with AcOH. A solid product separated which was extracted with ether and, after the usual treatment, gave 3-(4-amino-3,5-dimethylphenyl)-4-hydroxybenzophenone (**12**): yield 1.2 g; mp 162 °C (*i*-PrOH). More **12** was obtained from the phosphoric aqueous solution: ^1H NMR 7.8 (7 H, m, aromatic in positions 2′ and 4′ and C_6H_5CO), 7.25 (2 H, s, aromatic in positions 2 and 6), 7.17 (1 H, d, aromatic in position 5′), 3.63 (2 H, br s, exchangeable with D_2O, NH_2), 2.23 (6 H, s, 2 CH_3).

Registry No. **1**, 75475-99-9; **2**, 75476-00-5; **3**, 75476-01-6; **4**, 75476-02-7; **5**, 75476-03-8; **6**, 75476-04-9; **7**, 75476-05-0; **8**, 75476-06-1; **9**, 75476-07-2; **10**, 75476-08-3; **11**, 75476-09-4; **12**, 75476-10-7; 3,5-dimethyl-4-hydroxyacetophenone, 5325-04-2; (2,6-dimethylphenyl)hydrazine, 603-77-0; 2,6-dimethyl-4-fluoronitrobenzene, 315-12-8; 3,5-dimethylfluorobenzene, 461-97-2; 4-hydroxyacetophenone, 99-93-4; (3,5-dimethylphenyl)hydrazine, 39943-61-8; 3,5-dimethyl-4-hydroxybenzophenone, 5336-56-1; 4-hydroxybenzophenone, 1137-42-4.

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α-Silicon- and α-Alkynyl-Substituted Vinyl Cations

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The solvolytic reactivity of a number of silicon- and alkynyl-substituted vinyl triflates was investigated in aqueous ethanol. Activation parameters and solvent *m* values were determined for all substrates. Relative rate data show that the Me_3Si group is accelerating and hence stabilizing relative to hydrogen but destabilizing relative to a *t*-Bu group. The α-ethynyl substituent causes a rate decrease compared to a methyl group despite its π-donating resonance ability. These results are discussed.

Diverse evidence suggests a dichotomous donor-acceptor behavior for trialkylsilyl groups.[1a] It is well established that an α-$(CH_3)_3Si$ group imparts considerable stability to a carbanion.[1b] The effect of silicon substitution on the

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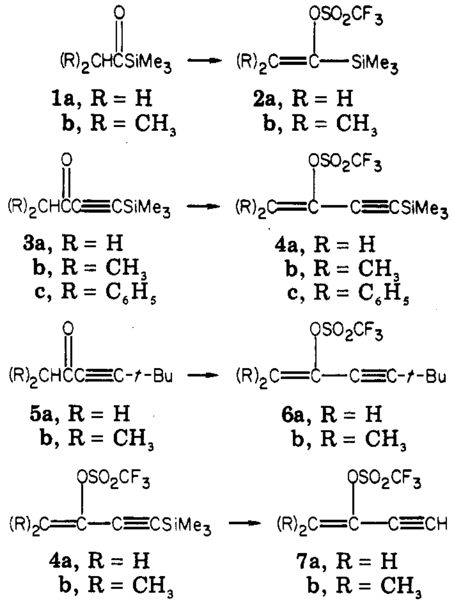
stability of carbenium ions is less investigated and understood although a number of studies[2] indicate that β-silicon substitution provides stabilization and α-substitution destabilization of these electron-deficient intermediates.

Recent interest in vinyl cations[3] prompted us to study the effect of silicon substitution on such unsaturated cations. To date, indirect evidence via the participation of the (trimethylsilyl)acetylenic group in polyene cyclizations[4,5] suggests that α-silicon substitution destablizes vinyl cations. We chose to investigate this question by means of direct solvolysis of α-silyl-substituted vinyl triflates.

Similarly, theoretical[6] as well as experimental[7] data indicate that the triple bond destabilizes carbenium ions; i.e., propargyl systems react slower than the corresponding n-propyl substrates despite the resonance stabilization of the propargyl cation. Recent theoretical studies[8] indicate that α-alkynyl substitution should destablize vinyl cations as well. Preliminary data of Taniguchi[9] and Hanack[10] and their co-workers give conflicting results with alkynyl substitution being destabilizing in the case of arylvinyl cations and seemingly stabilizing in simple alkylvinyl cations.[10] Therefore we investigated the solvolysis of several α-alkynyl-substituted vinyl triflates along with appropriate model compounds.

Results and Discussion

α-Silylvinyl triflates **2** were prepared from the corresponding silyl ketones **1** as previously reported.[11] Similarly (trimethylsilyl)alkynylvinyl triflates **4** were prepared from the corresponding ketones **3** as previously described.[12] Model compounds **6** were prepared by an analogous procedure from the appropriate ketones **5**. Finally, α-ethynylvinyl triflates **7** were prepared from the silated precursors **4** via desilylation with KF in methanol as previously reported.[12]



$(R)_2CHC(=O)SiMe_3 \longrightarrow (R)_2C{=}C(OSO_2CF_3){-}SiMe_3$

1a, R = H
b, R = CH$_3$

2a, R = H
b, R = CH$_3$

$(R)_2CHC(=O)C{\equiv}CSiMe_3 \longrightarrow (R)_2C{=}C(OSO_2CF_3){-}C{\equiv}CSiMe_3$

3a, R = H
b, R = CH$_3$
c, R = C$_6$H$_5$

4a, R = H
b, R = CH$_3$
c, R = C$_6$H$_5$

$(R)_2CHC(=O)C{\equiv}C\text{-}t\text{-Bu} \longrightarrow (R)_2C{=}C(OSO_2CF_3){-}C{\equiv}C\text{-}t\text{-Bu}$

5a, R = H
b, R = CH$_3$

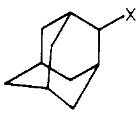
6a, R = H
b, R = CH$_3$

$(R)_2C{=}C(OSO_2CF_3){-}C{\equiv}CSiMe_3 \longrightarrow (R)_2C{=}C(OSO_2CF_3){-}C{\equiv}CH$

4a, R = H
b, R = CH$_3$

7a, R = H
b, R = CH$_3$

Rates of solvolyses of vinyl triflates **2**, **4**, **6**, and **7** were measured in duplicate conductometrically in unbuffered aqueous ethanol. Excellent first-order rates were obtained in all instances to better than 95% reaction; the data together with activation parameters and solvent m values are summarized in Table I. The solvent m values, activation parameters, and first-order rate constants reported in Table I with the exception of **2a** all are consistent with the direct solvolytic generation of the respective intermediate vinyl cation.[3] It is well-known that m values for triflate solvolysis for both alkyl[13] and vinyl[3] substrates tend to be low, in the 0.40–0.80 range, a phenomenon ascribed to the decreased solvation requirements of the triflate anion.[13] This novel suggestion of Creary's is supported by the decrease in solvent m value from 1.03 to 0.91 in the solvolysis of adamantyl bromide **8a** compared to the tosylate **8b** and a further decrease to m = 0.60 for the triflate **8c** in line with the increasing leaving abilities of these groups.[13] The unusually fast rate of reaction as well as the very low solvent m value of only 0.28 for **2a** strongly suggests a different mode of reaction for this simple silylvinyl triflate, most likely an E2-type elimination with solvent acting as a base. Hence the faster reaction of the silyl system **2a** compared to the model compound **10** may not be a reliable indicator of the true effect of silicon substitution on vinyl cation formation.



8a, X = Br
b, X = p-CH$_3$C$_6$H$_4$SO$_3$
c, X = CF$_3$SO$_3$

The effect of silyl as well as α-alkynyl substitution is best discussed by means of the relative rates summarized in Tables II and III. It is evident from the data in Table II that *relative to hydrogen* (entries 5 and 6) as well as methyl (entries 1 and 3) a trimethylsilyl group accelerates the rate of reaction of vinyl triflates and hence seems to stabilize the intermediate vinyl cations. This suggests that relative to hydrogen the Me$_3$Si group is electron donating, in accord with the data on the gas-phase basicities of silylamines[1a] as well as the theoretical calculations of Apeloig, Schleyer, and Pople.[14] However, if the *tert*-butyl group is taken as a model a different conclusion emerges. As entry 4 of Table II suggests [(CH$_3$)$_2$C=C(OTf)-t-Bu

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Table I. Rates of Solvolyses, Solvent *m* Values, and Activation Parameters for Silyl- and Alkynylvinyl Triflates

compd	temp, °C	solvent[a]	k, s^{-1} [b]	*m*	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu (25 °C)
$H_2C=C(OTf)SiMe_3$	25.0	50E	1.64×10^{-4} [c]			
2a	35.24 ± 0.01	80E	$(2.079 \pm 0.033) \times 10^{-4}$	0.28	23.2	−0.2
	35.24 ± 0.01	90E	$(1.275 \pm 0.004) \times 10^{-4}$			
	44.94 ± 0.01	80E	$(6.79 \pm 0.15) \times 10^{-4}$			
$(CH_3)C=C(OTf)SiMe_3$	25.0	50E	6.34×10^{-5} [c]			
2b	35.28 ± 0.01	70E	$(1.007 \pm 0.023) \times 10^{-4}$	0.46	28.3	15.2
	35.28 ± 0.01	80E	$(5.33 \pm 0.018) \times 10^{-5}$			
	44.96 ± 0.01	70E	$(4.674 \pm 0.044) \times 10^{-4}$			
$H_2C=C(OTf)C\equiv CSiMe_3$	25.0	50E	1.53×10^{-6} [c]			
4a	65.09 ± 0.03	50E	$(2.821 \pm 0.005) \times 10^{-4}$	0.55	25.6	−0.6
	65.09 ± 0.03	60E	$(1.436 \pm 0.002) \times 10^{-4}$			
	75.13 ± 0.01	70E	$(4.404 \pm 0.092) \times 10^{-4}$			
$(CH_3)_2C=C(OTf)C\equiv CSiMe_3$	25.0	50E	2.82×10^{-7} [c]			
4b	65.09 ± 0.03	50E	$(6.60 \pm 0.003) \times 10^{-5}$	0.64	26.7	−0.3
	65.09 ± 0.03	60E	$(3.03 \pm 0.003) \times 10^{-5}$			
	75.13 ± 0.04	60E	$(9.76 \pm 0.006) \times 10^{-5}$			
$(C_6H_5)_2C=C(OTf)C\equiv CSiMe_3$	25.0	50E	6.09×10^{-8} [c]			
4c	75.19 ± 0.05	50E	$(4.06 \pm 0.031) \times 10^{-5}$	0.49	26.2	−4.8
	75.19 ± 0.05	60E	$(2.24 \pm 0.001) \times 10^{-5}$			
	85.85 ± 0.05	60E	$(6.61 \pm 0.052) \times 10^{-5}$			
$H_2C=C(OTf)C\equiv CBu\text{-}t$	25.0	50E	7.83×10^{-5} [c]			
6a	44.93 ± 0.01	70E	$(2.702 \pm 0.018) \times 10^{-4}$	0.55	23.7	−2.0
	44.93 ± 0.01	80E	$(1.264 \pm 0.036) \times 10^{-4}$			
	55.02 ± 0.01	80E	$(4.078 \pm 0.055) \times 10^{-4}$			
$(CH_3)_2C=C(OTf)C\equiv CBu\text{-}t$	25.0	50E	1.37×10^{-5} [c]			
6b	44.93 ± 0.01	70E	$(5.28 \pm 0.001) \times 10^{-5}$	0.59	25.7	+2.7
	55.00 ± 0.02	70E	$(1.880 \pm 0.003) \times 10^{-4}$			
	55.00 ± 0.02	80E	$(8.43 \pm 0.005) \times 10^{-5}$			
$H_2C=C(OTf)C\equiv CH$	25.0	50E	4.99×10^{-8} [c]			
7a	75.13 ± 0.04	50E	$(2.37 \pm 0.007) \times 10^{-5}$	0.52	24.8	−8.6
	75.13 ± 0.04	60E	$(1.26 \pm 0.001) \times 10^{-5}$			
	85.65 ± 0.03	50E	$(6.62 \pm 0.007) \times 10^{-5}$			
$(CH_3)_2C=C(OTf)C\equiv CH$	25.0	50E	4.63×10^{-9} [c]			
7b	75.13 ± 0.01	50E	$(5.46 \pm 0.02) \times 10^{-6}$	0.54	28.7	−0.5
	85.65 ± 0.03	50E	$(1.78 \pm 0.003) \times 10^{-5}$			
	85.65 ± 0.03	60E	$(9.22 \pm 0.002) \times 10^{-6}$			
$H_2C=C(OTf)CH_3$ [d]	25.0	50E	7.14×10^{-7} [c]			
9	75.0	50E	3.31×10^{-4}		24.7	−3.7
	50.2	50E	1.95×10^{-5}			
$H_2C=C(OTf)Bu\text{-}t$ [d]	25.0	50E	2.65×10^{-6} [c]			
10	75.0	50E	8.78×10^{-4}		23.3	−5.7
	50.4	50E	6.03×10^{-5}			
$(CH_3)_2C=C(OTf)CH_3$ [d]	25.0	50E	5.35×10^{-7}			
11	100.0	80E	3.33×10^{-4}	0.61	25.5	−3.4
	100.0	60E	1.64×10^{-3}			
	100.0	50E	2.82×10^{-3}			
	75.0	80E	2.70×10^{-5}			
	75.0	60E	1.31×10^{-4}			
	75.0	50E	2.94×10^{-4}			
$(CH_3)_2C=C(OTf)Pr\text{-}i$ [d]	25.0	50E	8.51×10^{-5}			
12						

[a] Aqueous ethanol. [b] Average of duplicate runs. [c] Extrapolated. [d] Data from: Summerville, R. H., et al. *J. Am. Chem. Soc.* **1974**, *96*, 1100–1110.

Table II. Relative Rates of Reaction of α-Silyl and α-Alkynylsilyl Vinyl Triflates at 25 °C in 50% EtOH

entry	compd	10^5k_1, s^{-1}	compd	10^5k_2, s^{-1}	k_1/k_2
1	$CH_2=C(OTf)SiMe_3$ **2a**	16.4	$CH_2=C(OTf)CH_3$ **9**	0.0714	229
2	**2a**	16.4	$CH_2=C(OTf)t\text{-}Bu$ **10**	0.265	62
3	$(CH_3)_2C=C(OTf)SiMe_3$ **2b**	6.34	$(CH_3)_2C=C(OTf)CH_3$ **11**	0.0535	118
4	**2b**	6.34	$(CH_3)_2C=C(OTf)i\text{-}Pr$ **12**	8.51	0.75
5	$CH_2=C(OTf)C\equiv CSiMe_3$ **4a**	0.153	$CH_2=C(OTf)C\equiv CH$ **7a**	4.99×10^{-3}	31
6	$(CH_3)_2C=C(OTf)C\equiv CSiMe_3$ **4b**	0.0282	$(CH_3)_2C=C(OTf)C\equiv CH$ **7b**	4.63×10^{-4}	61
7	**4a**	0.153	$CH_2=C(OTf)C\equiv CBu\text{-}t$ **6a**	7.83	0.019
8	**4b**	0.0282	$(CH_3)_2C=C(OTf)C\equiv CBu\text{-}t$ **6b**	1.37	0.021

Table III. Relative Rates of Reaction of α-Alkynyl Vinyl Triflates at 25 °C in 50% EtOH

entry	compd	10^6k_1, s^{-1}	compd	10^6k_2, s^{-1}	k_1/k_2
1	$CH_2{=}C(OTf)CH_3$ **9**	0.714	$CH_2{=}C(OTf)C{\equiv}CH$ **7a**	0.0499	14.3
2	$(CH_3)_2C{=}C(OTf)CH_3$ **11**	0.535	$(CH_3)_2C{=}C(OTf)C{\equiv}CH$ **7b**	0.00463	115
3	$CH_2{=}C(OTf)C{\equiv}CBu$-*t* **6a**	78.3	**9**	0.714	109
4	$(CH_3)_2C{=}C(OTf)C{\equiv}CBu$-*t* **6b**	13.7	**11**	0.535	25.6

unfortunately cannot be made by any known method hence the *i*-Pr is used instead] and entries 7 and 8 confirm the $SiMe_3$ group is deactivating compared to *t*-Bu. Since the relative steric factors of the *t*-Bu and the Me_3Si groups, due to the shorter C–C bonds compared to the C–Si bond (1.54 Å vs. 1.88 Å),[15] are presumably minimized in the respective alkynylvinyl substrate, the reactivity ratio of 50 (entries 7 and 8) suggests a destabilizing influence of the Me_3Si group (relative to *t*-Bu) in accord with the indirect data from polyene cyclizations.[4,5] Hence one may conclude that in a situation of considerable electron demand such as a vinyl cation, unlike in carbenium ions, α-silicon substitution results in stabilization. However, the stabilizing effect of a Me_3Si group is not as effective as that of a *t*-Bu group.

Similarly, it is evident from entries 1 and 2 in Table III that the parent ethynyl group is destabilizing compared to a methyl group. This is in accord with the findings of Hanack[10] as well as the theoretical predictions of Apeloig et al.[8] and has been correctly ascribed to the greater inductive withdrawing effect of the triple bond compared to its resonance-stabilizing effect.[8] Indeed in the case of the unsubstituted ethynyl group the extended cumulenyl resonance form **13b** of the intermediate vinyl cation **13** (R = H) would in fact be a "primary" system that would not be expected to be very stable. Further substitution of the triple bond stabilizes form **13b** and as expected (entries 3 and 4, Table III) accelerates the rate of reaction compared to a simple methyl group.

13a **13b**

Finally, with the exception of silylvinyl triflate **2b** no product studies were carried out in these systems as both Taniguchi[9] and Hanack[10] have already demonstrated that the expected cumulenyl-derived, **13b**, products do not survive the reaction conditions and the remaining products are unexceptional. In the case of silylvinyl triflate **2b** at 75 °C in 50% EtOH, as anticipated, the only product observed by gas chromatography was the silyl ketone **1b**.

In summary, we have shown that silicon substitution on a vinylic substrate stabilizes the intermediate vinyl cation but less effectively than a *t*-Bu group. In contrast the α-ethynyl group destabilizes a vinyl cation just as it does a carbenium ion, despite its π-donating resonance ability.

Experimental Section

Boiling points and melting points are uncorrected. Infrared spectra were recorded on a Beckman IR5A or Acculab 3 spectrophotometer calibrated to the 1601.8-cm^{-1} line of polystyrene film. Proton NMR were recored on a Varian EM-360 or EM-390 spectrometer. Preparative GC was done on a Varian-Aerograph 90-P or 920 gas chromatograph. Solvents and reagents were purified and dried by standard procedures immediately prior to use.

Preparation of Vinyl Triflates 2, 4, 6, and 7. Vinyl triflate **2b** was prepared and characterized as previously reported.[11] Vinyl triflate **2a** was similarily prepared from known[16] $CH_3COSiMe_3$. A 0.9-g (7.8 mmol) portion of ketone **1a** gave 0.5 g (52%) of **2a** as pale yellow oil: IR (neat) 1623 (C=C), 1420, 1259, 1220, 1160, 939 (CF_3SO_3), 860 cm^{-1} (Me_3Si); NMR ($CDCl_3$) 0.17 (9 H, s, Me_3Si), 5.16 (1 H, d, *J* = 4.0 Hz), 5.77 ppm (1 H, d, *J* = 4.0 Hz).

Vinyl triflates 4 and 7 were prepared as previously reported.[12] Vinyl triflates **6a** and **6b** were prepared in a similar manner as described below.

Preparation of Ketones 5a and 5b. *t*-$BuC{\equiv}CSiMe_3$ was prepared by interaction of *t*-$BuC{\equiv}CH$ with *n*-BuLi in THF at −78 °C followed by quenching with Me_3SiCl: bp 76–80 °C (145 torr); IR (neat) 2160 (C≡C), 840 cm^{-1} (Me_3Si). To this acetylene, 4.5 g (29 mmol), in 150 mL of CH_2Cl_2 cooled to 0 °C were added 2.3 g (29 mmol) of acetyl chloride followed by 4.3 g (32 mmol) of $AlCl_3$. Workup was as previously described,[12] yielding 2.3 g (64%) of ketone **5a**: bp 90–98 °C (120–123 torr); IR (neat) 2230 (C≡C), 1680 cm^{-1} (C=O). Similarly 3.0 g (68%) of ketone **5b** was obtained from 29 mmol of *t*-$BuC{\equiv}CSiMe_3$ interacting with 29 mmol of isobutyryl chloride: bp 115–119 °C (125 torr); IR (neat) 2220 (C≡C), 1675 cm^{-1} (C=O).

Preparation of Vinyl Triflates 6a and 6b. Ketones **5a** (18 mmol) and **5b** (20 mmol), respectively, were each reacted with a 20% excess of triflic anhydride under previously reported conditions[12] to give upon workup **6a** (53%) [IR (neat) 2215 (C≡C), 1630 (C=C), 1430, 1220, 1140, 935 cm^{-1} (CF_3SO_3); NMR ($CDCl_3$, internal Me_4Si) 1.21 (s, 9 H, *t*-Bu), 5.3 ppm (m, 2 H, $C{=}CH_2$)] and **6b** [77%; IR (neat) 2210 (C≡C), 1660 (C=C), 1425, 1220, 1150, 950 cm^{-1} (CF_3SO_3); NMR ($CDCl_3$, internal Me_4Si) 1.25 (s, 9 H, *t*-Bu), 1.81 (s, 3 H, CH_3), 1.89 ppm (s, 3 H, CH_3)]. Both vinyl triflates **6a** and **6b** are stable at 0 °C for several weeks; however, at room temperature they turn colored and slowly decompose in 2–4 days.

Kinetic and Product Studies. Rate constants were obtained conductimetrically as previously described.[17] Product studies were performed on 0.02 M triflate **2b** in 50% ethanol at 75 °C. Gas chromatographic analysis (Se-30, 10 ft × 0.125 in., 100 °C) of the reaction mixture after 5 half-lives indicated ketone **1b** as the sole product by comparison with authentic sample.

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Registry No. **1a**, 13411-48-8; **2a**, 75700-31-1; **2b**, 73876-87-6; **4a**, 71451-03-1; **4b**, 71451-04-2; **4c**, 71451-05-3; **5a**, 10564-81-5; **5b**, 18205-46-4; **6a**, 74142-32-8; **6b**, 75700-32-2; **7a**, 71451-06-4; **7b**, 71451-07-5; **9**, 24541-32-0; **10**, 27701-32-2; **11**, 28143-80-8; **12**, 52149-35-6; *t*-$BuC{\equiv}CSiMe_3$, 14630-42-3.

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