(22) O. Ermer and S. Lifson, *J. Am. Chem. Soc.*, **95**, 4121 (1973).
(23) G. Barbarella, unpublished.
(24) J. B. Stothers and N. Wilson, *Top. Stereochem.*, **8**, 1 (1974); J. B. Lambert and S. I. Featherman, *Chem. Rev.*, **75**, 611 (1975).
(25) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967); D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967).
(26) That in **3** the Me group has a shielding effect on the γ carbons is confirmed by the ^{13}C NMR spectrum of unsubstituted *trans*-thiacyclooct-4-ene: δ_{C_4} 130.4 and 37.8 $\geq \delta_{C_8} \geq$ 34.8, downfield with respect to **3**.[6]
(27) E. V. Whitehead, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3632 (1951).
(28) The assignment of C_8 was made on the basis of the residual splitting and as such cannot be considered absolutely certain. However, if the 25.9-ppm resonance were not assigned to C_8 it would have to be assigned to either C_7 or C_6. This would imply a δ effect, respectively twice an ϵ effect, on the order of 7 ppm, either of which would be completely unprecedented.

Preparation and Chemistry of Vinyl Triflates. 16. Mechanism of Alkylation of Aromatic Substrates[1,2]

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Abstract: The mechanism of electrophilic aromatic substitution with vinyl triflates was investigated. Alkylation of a series of monosubstituted benzenes gave a ρ value of -2.57, one of the lowest observed in any electrophilic aromatic substitution. Cyclooctenyl and cycloheptenyl triflates alkylated anisole, but cyclohexenyl triflate did not. All alkylations were carried out in the presence of 2,6-di-*tert*-butyl-4-methylpyridine, a sterically hindered nonnucleophilic base. These data are interpreted via a vinyl cation as the intermediate electrophile. From these results it is concluded that a number of other aromatic substitutions with unsaturated progenitors such as certain vinyl halides, vinyl esters, and alkynes may also proceed via the intermediacy of vinyl cations.

The familiar Friedel-Crafts alkylation of aromatic substrates has been known for a century.[3] The reaction is well known to involve electrophilic attack by trisubstituted carbonium ions or carbonium-ion-like species derived from a variety of precursors such as alkyl halides, alcohols, olefins, and others with the aid of various Lewis and/or Brønsted acids as catalysts.[4] Similarly, electrophilic substitution by disubstituted sp-hybridized ions like acylium and nitronium ions is well established.[4] These latter species of course derive their existence from the considerable stabilization provided to the cationic center by the adjacent heteroatom lone-pair electrons.

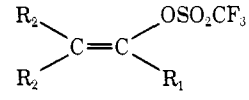
Considerable amount of work has also been done on aromatic alkylations with species derived from vinyl halides, vinyl esters, and alkynes catalyzed by Lewis or Brønsted acids. Shortly after the discovery of the Friedel-Crafts reaction Demole[5] and Anschütz[6] both reported the formation of 1,1-diphenylethene by alkylation of benzene with 1,1-dibromoethene and $AlCl_3$. Alkylation has also been reported with various other vinyl halides.[7-10] Similar alkylations have been observed with unsaturated esters such as Angelica lactone and vinyl acetates.[11-14] Alkynes and various mineral acids, both in the absence and presence of mercuric salts, have often been employed as precursors in aromatic alkylations.[15-19] In fact several efficient ring closures via alkylation, based upon protonation of alkynes, mostly by polyphosphoric acid, have been employed in the synthesis of certain heterocycles[20,21] as well as at least in one instance a steroid.[22]

Despite the plethora of experimental data on aromatic alkylations with unsaturated precursors, very little is known about the mechanism of these reactions. Such alkylations could proceed via disubstituted sp-hybridized vinyl cations[23] analogous to acylations and nitrations or by a different, unknown process. Exact mechanistic interpretation of these reactions is difficult not only for lack of appropriate data but also due to complications arising from the use of heterogeneous catalysts and reaction conditions, the presence of acid, and the possibility of product rearrangements.

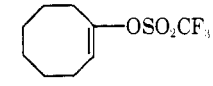
Hence, in order to unambiguously ascertain the feasibility of electrophilic aromatic substitution by vinyl compounds and in particular to assess the possible involvement of vinyl cations and the exact mechanism of such reactions we undertook a careful and detailed study of Friedel-Crafts alkylation with vinyl sulfonate esters.

Results and Discussion

It has long been known[24-28] that alkylations can be carried out in the absence of added Friedel-Crafts catalyst by use of alkyl sulfonate esters as carbonium ion precursors, thereby avoiding the usual complications due to heterogeneous reactions conditions. In order to increase the reactivity of normally lethargic vinylic compounds we prepared highly reactive vinyl triflates **1-6** as potential alkylating agents. Vinyl triflates **1-6**



1, $R_1 = R_2 = C_6H_5$
2, $R_1 = C_6H_5$; $R_2 = CH_3$
3, $R_1 = R_2 = CH_3$



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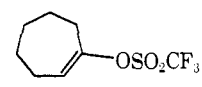

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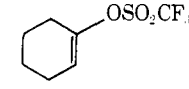

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were prepared in good yields from the appropriate ketones; in the case of **1** and **2** by trapping the KH-derived enolate[29] with triflic anhydride, and triflates **3-6** via known[30] literature procedures.

In order to avoid complications due to the acid liberated in all Friedel-Crafts alkylations, in the present case triflic acid, a base was sought that would neutralize the acid as rapidly as possible. To keep the reaction medium homogeneous, inorganic bases such as NaH, $NaHCO_3$, and Na_2CO_3 were avoided. Furthermore, to stop any interaction between potential electrophilic intermediates and base, thereby thwarting alkylation, sterically hindered nonnucleophilic bases were desirable. 2,6-Di-*tert*-butyl-4-methylpyridine (**7**) proved to be ideal owing to its ready availability,[31] deactivated aromatic ring, and

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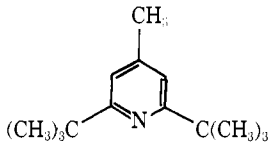
Table I. Alkylation of Aromatic Substrates with Vinyl Triflates

Starting triflate	Aromatic substrate and rxn conditions	Products, yield[a]
1	C_6H_6, 150 °C, 24 h	$(C_6H_5)_2C{=}C(C_6H_5)_2$, 54%
2	$C_6H_5OCH_3$, 120 °C, 24 h	$(CH_3)_2C{=}CC_6H_5(C_6H_4OCH_3)$,[b] 79%
3	C_6H_6, 80 °C, 48 h	No rxn, **3** recovered
3	C_6H_6, 80 °C, BF_3, 48 h	No rxn, **3** recovered
3	C_6H_6, 150 °C, 12 h	Tar
4	$C_6H_5OCH_3$, 155 °C, 20 h	1-(*p*-Methoxyphenyl)cyclooctene, 21%
5	$C_6H_5OCH_3$, 170 °C, 24 h	1-(*p*-Methoxyphenyl)cycloheptene, 30%
6	$C_6H_5OCH_3$, 280 °C, 48 h	No rxn, **6** recovered

[a] Isolated yields, >98% pure by GC. [b] Mixture of ortho and para isomers.

ability to interact rapidly with protons but not larger species[32] such as BF_3 or CH_3I and hence any latent cations. Preparative alkylations were carried out in sealed tubes with 2-3 mmol of vinyl triflate in a 20-40-fold excess of anhydrous aromatic substrate in the presence of 1-2 equiv of base **7**. Reaction



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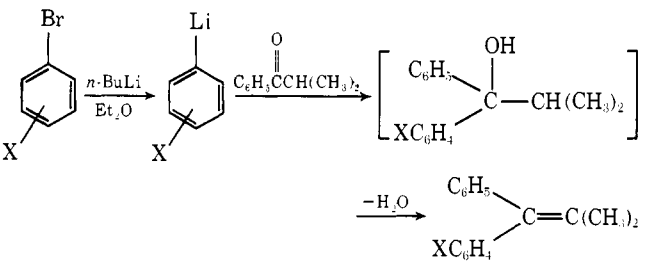
mixtures were worked up by dilution with pentane, filtration of the precipitated pyridinium triflate, evaporation of the solvent, and vacuum distillation of the residual oil in a microstill. Products were identified by spectral means, or were available by GC and spectral comparison with authentic samples. The results are given in Table I.

Having established that vinyl triflates indeed alkylate aromatic substrates we set out to determine the inter- as well as intramolecular selectivity of these reactions. In order to determine these selectivities vinyl triflate **2** was reacted with a large excess of a known mixture of a substituted benzene and benzene itself in the presence of excess base **7** and an inert internal standard for 24 h at 120 °C. Reactions were run in duplicate and the products GC analyzed with the aid of authentic samples. Authentic samples were independently synthesized by the procedure shown in Scheme I. An appropriately sub-

Scheme I. Preparation of Authentic Substituted Styrenes 8



8

stituted aryl bromide was exchanged with n-C_4H_9Li, the resulting aryllithium compound was reacted with isobutyrophenone, and the product alcohol was dehydrated to the desired styrene **8**. Relative reactivities were calculated by means of well-established relationships[33] and are summarized in Table II together with other relevant data.

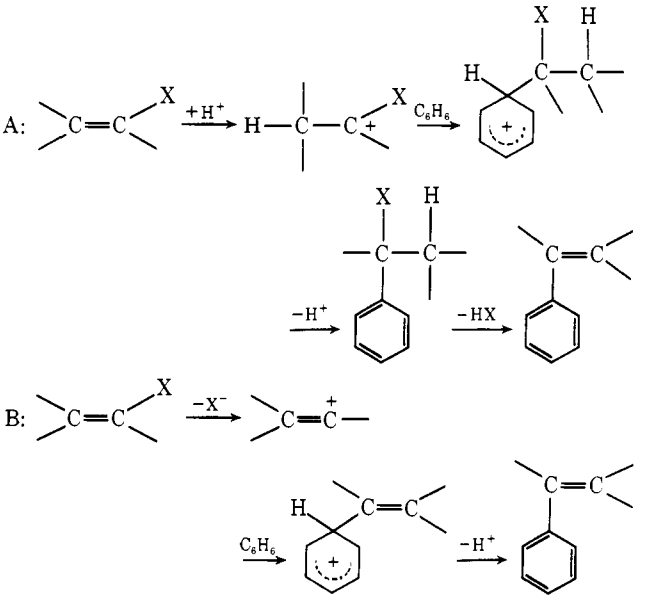
In order to further probe the mechanism of Friedel-Crafts alkylations with vinyl triflates an isotope effect determination was also carried out by competitive alkylation of C_6D_6 and C_6H_6; a $k_H/k_D = 0.98 \pm 0.026$ was observed.

Mechanistic Considerations. Electrophilic aromatic substitution with any vinyl progenitor may occur by one of two pathways as shown in Scheme II.

Table II. Isomer Distribution and Relative Reactivity of Vinyl Triflate **2** with Monosubstituted Benzenes at 120 °C

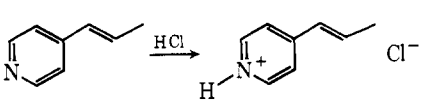
X	Yield of **8**, %	% composition of **8**			k_{rel}
		o-	*m*-	*p*-	
CH_3O	85	11.3	0.0	88.7	118.5
CH_3	66.4	27.6	8.0	63.6	6.76
F	87.0	21.1	0.0	78.9	2.00
H	79.0				1.00
Cl	80.0	29.7	0.0	70.3	0.63

Scheme II. Mechanisms of Electrophilic Aromatic Substitution with Vinyl Compounds



Path A involves initial protonation of the olefinic π bond and alkylation by the resultant carbonium ion, followed by elimination of HX to give the observed styrene products. Path B involves prior ionization to a vinyl cation and direct formation of the styrene products by electrophilic substitution via such vinyl cation intermediates.

We believe that our experimental observations with vinyl triflates are consistent only with path B and the involvement of vinyl cations in electrophilic aromatic substitution. This conclusion is based on the following considerations. Alkylation occurs even in the presence of an amine base **7** that should rapidly neutralize any acid present. The pK_a of **7** is 4.41 in 50% ethanol[34] comparable to $pK_a = 4.38$ for pyridine itself.[35] Pyridine bases such as 4-alkylpyridine **9** react with HCl to form a salt **10** with no addition to the double bond being observed.[36]



9 **10**

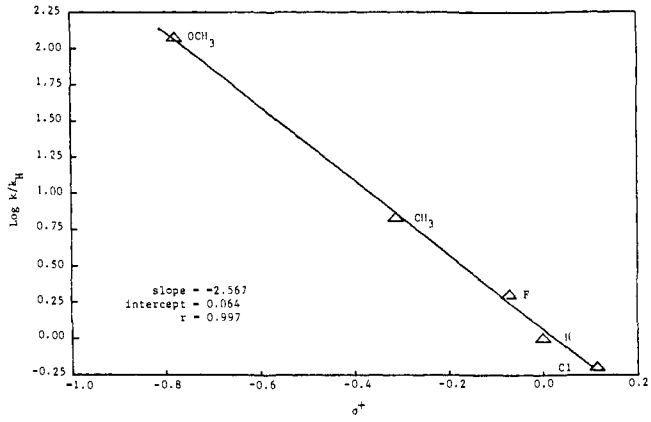


Figure 1. Log k/k_H vs. σ^+.

The reactivity of the cyclic vinyl triflates **4-6** is highly informative concerning the nature of the electrophilic species involved in these alkylations. Protonation of the three cyclic triflates should occur under comparable conditions since the intermediate carbonium ions should be nearly strainless and Olah and Spear[37] have shown that vinyl fluorosulfonates can be readily protonated upon treatment with FSO_3H. Subsequent alkylation by the resultant carbonium ions should also be comparable. Yet, as the data in Table I indicate, cycloheptenyl triflate **5** needs more stringent reaction conditions for alkylation to occur than cyclooctenyl triflate **4** and cyclohexenyl triflate **6** does not alkylate at all even after 48 h at 280 °C. Rather, these reaction conditions, at least qualitatively, resemble the solvolytic behavior of vinyl triflates **4-6** known[23,38] to involve vinyl cation intermediates. Hence the failure of the cyclohexenyl triflate **6** to alkylate an aromatic ring can be explained by the high strain energy involved in the bent vinyl cation[23] necessary for alkylation to have occurred. The solvolysis of **6** in aqueous ethanol, a much more polar medium than anisole, was found to be some 10^4 times slower than that of **5**.[38]

The data in Table II are equally instructive. The relative reactivity data are best represented as a Hammett plot of log k_X/k_H vs. Brown's[39,40] σ^+, given in Figure 1. The negative ρ value clearly indicates an electrophilic intermediate but the magnitude of only −2.57 is one of the lowest observed when compared to other electrophilic substitutions as summarized in Table III. Such a low ρ value clearly argues for a highly reactive and hence intermolecularly nonselective electrophilic intermediate, such as a vinyl cation. In fact the only less selective reaction seems to be ethylation via ethyl cations and vinyl cations are known[23] to be comparable in energy to ethyl cations. This low value of ρ further rules out protonation and subsequent alkylation by normal carbonium ions. Protonation of triflate **2** would have resulted in a benzyl cation and the ρ value for benzylation of aromatic substrates using benzyl tosylate as a cation progenitor is known to be $\rho = -4.17$.[43]

However, as the product isomer distribution data in Table II indicate, this low intermolecular selectivity does not translate into a comparable intramolecular nonselectivity. In fact, rather than the statistically expected distribution of product isomers, i.e., 40% ortho, 40% meta, and 20% para, likely to occur from a completely nonselective reaction, a highly selective product distribution was observed. With the aid of authentic samples and analytical GC less than 0.1% of meta isomer would have been detected, yet, except for toluene, none was observed. Hence one is faced with the dilemma of explaining how an intermolecularly nonselective species (low ρ) acquires such great intramolecular selectivity if both inter- and intramolecular selectivity are determined in the same transition state. This dilemma can be resolved by postulating the existence of two transition states prior to the formation of the usual σ complex. The first transition state determines the intermolecular selectivity (ρ) and the second transition state determines the intramolecular selectivity (isomer distribution). The low value of ρ indicates that the alkylating agent shows little differentiation between various monosubstituted aromatic rings, based upon the electron-donating or -withdrawing ability of the substituent. As an electrophilic species approaches an aromatic ring, electrons will flow out of the π cloud of the ring and toward the electrophilic species. The π cloud can be said to be disrupted to the extent that electrons are lost in the transition state. Since the substituent will act to stabilize the growing positive charge on the ring by electron donation, one would expect that the substituents most able to donate electrons (CH_3O, CH_3) would react much faster than substituents that are less able to donate electrons (H, Cl) to the disrupted π system. However, since all substituents react at similar rates (low ρ value), the π system must not be significantly disrupted in the transition state. Hence the first transition state must, therefore, resemble an "inner" π complex rather than a σ complex which involves a greater disruption of the π system. It should be noted that no meta substitution occurs for anisole or chloro- and fluorobenzene, but that 8% meta substitution occurs for toluene. This seeming departure from intramolecular selectivity can be explained by the signs of the σ^+ constants for the substituents concerned. The σ_m^+ values for Cl, F, and OCH_3 are positive, which indicates that the meta positions are deactivated by the substituent. The σ_m^+ for CH_3 is negative, indicating that the meta position of toluene is activated by the methyl group. In addition, the signs of σ_p^+ for all the substituents are negative; therefore, all the para positions are activated. Since product isomerizations were ruled out by control experiments (see Experimental Section), one can conclude that alkylation by vinyl cations occurs only on activated ring positions.[44a] Finally, an electron transfer and radical pair mechanism analogous to that proposed for nitration by Perrin[44b] might also account for the different inter- and intramolecular selectivities.

Table III. ρ Values for Electrophilic Aromatic Substitutions[a]

Rnx conditions	ρ[b]
Chlorination, Cl_2, HOAc, 25 °C	−10.0
Acetylation, CH_3COCl, $AlCl_3$, $C_2H_4Cl_2$, 25 °C	−9.1
Bromination, Br_2, HOAc; CH_3NO_2, 30 °C	−8.7
Mercuration, $Hg(OAc)_2$, HOAc, 25 °C	−4.0
Ethylation, EtBr, GaBr, ArH, 25 °C	−2.4

[a] Data from ref 42. [b] All against σ^+

The observed lack of a deuterium isotope effect is in accord with these hypotheses. Proton loss must occur after the rate-determining step and subsequent to the formation of the usual σ complex. The value of $k_H/k_D = 0.98$ is in accord with similar values of $k_H/k_D = 0.90$ and $k_H/k_D = 1.13$ for nitration[45] and benzylation,[46] respectively, and are accounted for by the Streitwieser[47] formulations.

The lack of alkylation with triflate **3** deserves comment. The fact that no reaction at all occurred under the milder reaction conditions is consistent with the higher energy and hence lower stability and accessibility of alkylvinyl cations compared to the aryl stabilized vinyl cations possible from **1** and **2**. At the higher reaction conditions only tar was observed. This probably arose via vinyl cation formation, loss of proton, and allene oligomerizations. Such eliminations and allene formation have been observed in the solvolysis of simple alkylvinyl triflates.[23] This would clearly seem to indicate that proton elimination from an intermediate vinyl cation is a more favorable process than alkylation of a relatively weakly nucleophilic aromatic system.[48] Hence only vinyl systems that do not possess β hydro-

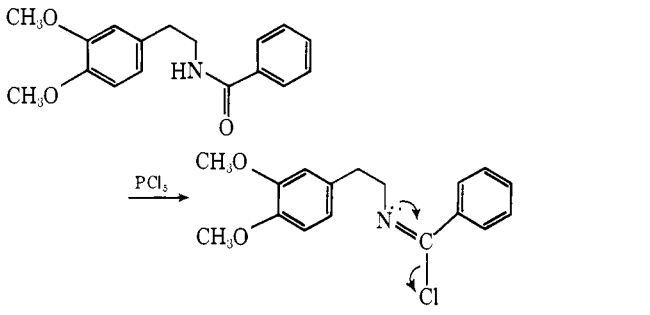
gens and/or are incapable of β-elimination can be used to alkylate aromatic substrates.

Summary

We have clearly established that vinyl triflates can alkylate aromatic substrates in the absence of any catalyst and the presence of a sterically hindered nonnucleophilic base. The observed ρ value of -2.57 strongly suggests a highly reactive and intermolecularly nonselective electrophilic intermediate such as a vinyl cation. This conclusion is supported by the behavior of the six-, seven-, and eight-membered cyclic vinyl triflates. The highly selective isomer distributions further suggest two distinct transition states for control of inter- and intramolecular selectivities. The observed $k_H/k_D = 0.98$ is in accord with deuterium isotope effects observed in normal electrophilic aromatic substitutions.

Furthermore, in retrospect, there is little doubt that vinyl cations may be involved as intermediates in many of the electrophilic aromatic substitutions with unsaturated precursors cited in the introduction. Precursors possessing good leaving groups and capable of yielding stabilized vinyl cations[50] such as styryl bromide probably react via the intermediacy of such species, as do alkynes capable of giving similarly stabilized vinyl cations via protonation. Hence most of the cyclizations[20-22] probably proceed by protonation of the alkyne and intramolecular alkylation by the resulting vinyl cation.

Moreover, it is possible that a series of well-established reactions such as the Bischler-Napieralski[51] ring closure of *N*-acyl-2-arylethylamines to dihydroisoquinolines long thought to occur via carbonyl protonation[52] might in fact proceed by intramolecular alkylation by a nitrogen stabilized vinyl cation **12**. Imidoyl chlorides **11**, which have been found to be intermediates in the ring closure,[53] have been shown to display initial first-order kinetics, ascribed to the formation of ion **12** in the rate-determining step.[54] Ion **12** has been trapped as a stable crystalline SbF_6^- salt and shown to subsequently ring close to **13** in solution.[55]



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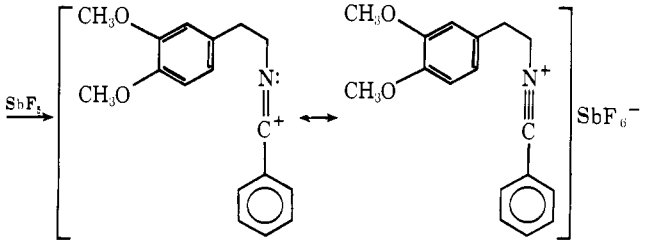

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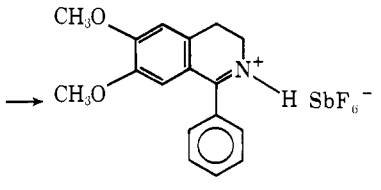

13

Similarly, the Gattermann formylation[56] using HCN and HCl, catalyzed by $ZnCl_2$, might proceed by way of the protonated species **14** as may the Hoesch acylation[57] using nitriles and HCl in the presence of $ZnCl_2$. Experiments testing these possibilities are underway.

$$[RC^+{=}\ddot{N}H \leftrightarrow RC{\equiv}N^+H]ZnCl_3^-$$

14, R = H, alkyl

Hence with the emergence of vinyl cations and related species as respectable members of the establishment of reactive intermediates[23] their involvement in a wide range of organic reactions is becoming ever more evident.

Experimental Section

General. All boiling points are uncorrected. Melting points were taken on a Thomas-Hoover melting point apparatus. Infrared spectra were recorded on either a Beckman IR5A or a Beckman Acculab 3 infrared spectrometer and are reported in wavenumbers (cm^{-1}) calibrated to the 1602-cm^{1} line of polystyrene. NMR spectra were recorded on a Varian A-60 or 360A spectrometer and are reported in parts per million (δ) downfield from internal Me_4Si. Mass spectra were recorded on a LKB Shimadzu 9000S gas chromatograph-mass spectrometer equipped with a 3 ft × 0.125 in. 1% OV-17 on 100/120 mesh Chromosorb Q column. All preparative GC was carried out on either a Varian Aerograph 90P or 920 gas chromatograph using a 5 ft × 0.25 in. 15% SF-96 on 60/80 Chromosorb W column. Analytical GC was carried out on a Hewlett-Packard 700 flame ionization GC coupled to a Hewlett-Packard 3370B digital integrator with either column A, 6 ft × 0.125 in. 10% UCW-982 on 100/120 Chromosorb W, or B, 57 ft × 0.125 in. 5% FFAP on 100/120 Chromosorb W.

Preparation of Vinyl Triflates 1-6. Vinyl triflates **1** and **2** were prepared from 2,2-diphenylacetophenone[58] and isobutyrophenone,[59] respectively, according to the following general procedure. Into a 100-mL three-necked round-bottom flask equipped with a constant-pressure addition funnel and magnetic stirrer and capped with two serum caps was weighed 1.50 g (19 mmol) of a 50% KH dispersion in mineral oil. The flask was flushed with a slow stream of dry N_2 via two syringe needles. The KH was washed four times with 20-mL portions of dry pentane in order to remove the mineral oil. Dry glyme (distilled from sodium benzophenone ketyl[60], 20 mL) was added with a syringe followed by the addition of 5 g (18.4 mmol) of 2,2-diphenylacetophenone in portions to moderate H_2 evolution. The contents of the flask turned to a brilliant yellow color, presumably owing to the enolate salt. After addition was complete the entire mixture was cooled to -70 °C by means of a dry ice/isopropyl alcohol bath. To the cooled solution 5.18 g (18.4 mmol) of triflic anhydride was added dropwise while vigorously stirring the reaction mixture. The yellow color was completely discharged after addition of all the anhydride. The mixture was allowed to warm to room temperature and the glyme was removed on a rotary evaporator at aspirator pressure with the aid of a water bath held at 40 °C. The residue was extracted with three 100-mL portions of pentane, the combined extracts were filtered, and the filtrate was evaporated on the rotary evaporator yielding 7.05 g (95%) of vinyl triflate **1**, mp 83-84 °C dec (lit.[61] mp 83.5-84 °C dec). Triflate **2** was similarly prepared from 14.8 mg (0.1 mol) of isobutyrophenone yielding 16 g (57%) of **2**: bp 60-61 °C (0.33 mm); NMR (CCl_4) δ 1.78 (s, 3), 1.99 (s, 3), 7.34 (s, 5); IR 952 and 888 cm^{-1} (OSO_2CF_3). Vinyl triflates **3-6** were prepared according to standard literature procedures.[30]

Preparation of Authentic Styrenes 8. All of the substituted styrenes **8** were prepared on the same scale from appropriately substituted bromobenzene and isobutyrophenone according to the following general procedure.

A 100-mL three-necked round-bottom flask was equipped with a nitrogen bubbler and magnetic stirrer bar and capped with serum caps. Freshly distilled *m*-bromotoluene (3.42 g, 0.02 mol) dissolved in 6 mL of dry ether was added and the solution cooled to -35 °C. With a syringe 8.33 mL (0.02 mol) of *n*-BuLi was added while stirring vigorously. The reaction mixture was stirred for 10 min at -35 °C and for 20 min at 0 °C, then a solution of 2.96 g (0.02 mol) of isobutyrophenone in 6 mL of dry ether was injected and the mixture stirred at room temperature for 20 min. The intermediate alcohol was isolated by pouring the reaction mixture into a 100-mL separatory funnel containing 20 mL of a 5% NH_4Cl solution, and extracted with 20 mL

Table IV. Spectral Properties of $XC_6H_4(C_6H_5)C{=}C(CH_3)_2$ (8)

X	NMR[a] CH_3	NMR[a] ArH	NMR[a] Other	IR, cm^{-1} [b] (C=C)	Mass spectrum[c]
m-CH_3	1.77 (m)	7.00 (m)	2.23 ($ArCH_3$)	1597	222 (100)
o-CH_3	1.60, 1.87	7.07 (m)	2.10 ($ArCH_3$)	1595	222 (65) 179
p-CH_3	1.77 (s)	7.07 (m)	2.20 ($ArCH_3$)	1590	222 (100)
m-Cl	1.80 (s)	7.10 (m)		1560	242 (100)
p-Cl	1.77 (s)	7.13 (m)		1590	242 (100)
m-F	1.77 (s)	6.92 (m)		1582	226 (100)
p-F	1.77 (s)	7.10 (m)		1502	226 (100)
m-CH_3O	1.78 (s)	6.67, 7.13	3.57 ($ArOCH_3$)	1592	238 (100)
o-CH_3O	1.63, 1.80	6.93	3.57 ($ArOCH_3$)	1597	238 (100)
1*p*-CH_3O	1.79 (s)	6.70, 7.21	3.56 ($ArOCH_3$)	1605	238 (100)
H	1.78 (s)	7.12 (s)		1603	208 (100)

[a] In CCl_4, internal Me_4Si = 0.0. [b] Neat. [c] First peak, molecular ion (%), second number base peak if not molecular ion.

Table V. Composition of Alkylation Solutions B_{1-4}

Solution	R	Wt C_6H_5R, g	Wt C_6H_6, g	Wt n-$C_{15}H_{32}$, g
B_1	CH_3	6.9103	2.0440	0.0037
B_2	Cl	8.3466	0.3155	0.0038
B_3	F	4.1255	0.7959	0.0032
B_4	CH_3O	0.4376	4.5587	0.0038

Table VI. Composition of Alkylation Samples

Sample	Wt of soln A, g	Wt of soln B, g
I-CH_3	0.0102	0.2335
I-Cl	0.0051	0.2623
I-F	0.0052	0.2891
I-CH_3O	0.0051	0.2344
II-CH_3	0.0052	0.2191
II-Cl	0.0054	0.2707
II-F	0.0051	0.2921
II-CH_3O	0.0051	0.2382

Table VII. Product Data and Competitive Rates

Substituent	GC response factor	Para/ parent	Log k_X/k_H
CH_3O	1.1687	1.3689	2.0736
CH_3	1.2725	2.9944	0.8300
F	1.1315	1.4012	0.3001
H	1.0734		
Cl	1.2601	1.9319	−0.1997

of pentane. The ether/pentane layer was extracted with 20 mL of saturated NaCl and the solvent was removed on the rotary evaporator. The residual oil was heated for 1 h at 180 °C with 1 g of freshly ground anhydrous oxalic acid. The residue was cooled and dissolved in 30 mL of pentane, and the pentane solution was washed with 20 mL of H_2O, 20 mL of 5% $NaHCO_3$, and 20 mL of saturated NaCl solution. After removal of the pentane on the rotary evaporator the residue was purified by preparative GC and identified by spectral means. Spectral properties of all styrenes **8** are reported in Table IV. Authentic alkylation products with cycloalkenyl triflates **4–6**, namely, 1-(*p*-methoxyphenyl)cyclooctene, 1-(*p*-methoxyphenyl)cycloheptene, and 1-(*p*-methoxyphenyl)cyclohexene, were similarly prepared from *p*-bromoanisole and the respective cycloalkenones and had spectral properties consistent with their structure.

General Alkylation Procedure. A mixture of 2–3 mmol of the appropriate vinyl triflate **1–6**, 1–2 equiv of base **7**, and a 20–30-fold excess of anhydrous aromatic substrate was sealed in a heavy-walled glass tube and heated at the indicated temperatures and period (Table I) in an oil bath. At the end of this period, where reactions occurred, a heavy crystalline precipitate of pyridinium triflate formed. The ampule was cooled, the contents were poured into pentane, and the pentane solution was filtered. The filtrate was evaporated on a rotary evaporator and the residual oil vacuum distilled in a microstill. Products were characterized by GC and spectral comparisons with commercial or previously prepared authentic samples. The results are given in Table I.

Competitive Alkylations. A solution of 0.1590 g (0.57 mmol) of triflate **2** and 0.1682 g (0.80 mmol) of base **7** was prepared and labeled A. Mixtures of known amounts of GC-pure anhydrous *n*-pentadecane, benzene, and a monosubstituted benzene were prepared and labeled solutions B_{1-4} (Table V).

Aliquots of solutions A and B were weighed into ampules in duplicate (series I and II of Table VI). The labeled sealed ampules were heated in an oil bath at 120 °C for 24 h. Each solution was analyzed four times and the results were averaged on an analytical GC. GC response factors, adduct ratios, and relative reactivities are given in Table VII. Relative reactivities were calculated by means of the relationship[33] $\log k_X/k_H = \log$ [6(para/parent) (mol C_6H_6/mol C_6H_5R)]. The distribution of ortho, meta, and para product isomers was also determined by means of authentic samples and is reported in Table II. A Hammett σ–ρ plot of the relative reactivity data is given in Figure 1.

Product Stability Determinations. Samples (20 mL) of authentic ortho, meta, and para styrenes **8** for each substituent were dissolved in the appropriate solution B. The mixtures were divided into two parts and placed in separate ampules. To one ampule from each group was added an excess of the triflic acid salt of base **7**; the other ampule was sealed, kept in a refrigerator, and used as a control. The ampule containing the pyridinium triflate salt was sealed and heated in an oil bath for 24 h at 120 °C. Both vials from each group were analyzed by analytical GC with no change in isomer ratio being observed for any substituent within experimental error.

Deuterium Isotope Studies. A mixture of 1.9508 g of C_6D_6 (Stohler Isotope Chemicals, lot 2616, 99.5% D) and 1.9567 g of C_6H_6 was mixed in a capped vial. A small portion of this mixture was sealed and set aside for mass spectral analysis. To the remaining mixture was added 0.6905 g (2.50 mmol) of triflate **2** and 0.5687 g (2.80 mmol) of base **7**. After complete mixing the solution was scaled in two ampules and each heated in an oil bath at 120 °C for 24 h. The products were analyzed by GC/mass spectrum, and found to contain D/H ratios of 0.8816 and 0.9088 for the duplicate samples, by total ion current determinations at the respective masses for 115 scans. Using the lot analysis, the starting ratio of H/D was 1.081 whereas by mass spectrum it was found to be H/D = 1.103 for an isotope effect of $k_H/k_D = 0.98 \pm 0.026$.

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References and Notes

(1) Part 15: P. J. Stang and A. G. Anderson, *Tetrahedron Lett.*, 1485 (1977).
(2) Abstracted in part from the Ph.D. dissertation of A. G. Anderson, The Uni-

versity of Utah, 1977.
(3) C. Friedel and J. M. Crafts, *Bull. Soc. Chim. Fr.*, **27**, 530 (1877); *C. R. Acad. Sci.*, **84**, 1392, 1450 (1877).
(4) G. A. Olah, "Friedel-Crafts and Related Reactions", Vol. 1–4, Wiley-Interscience, New York, N.Y., 1963–1964.
(5) E. Demole, *Ber.*, **12**, 2245 (1879).
(6) R. Anschütz, *Justus Liebigs Ann. Chem.*, **235**, 150 (1886).
(7) L. Schmerling, J. P. West, and R. W. Welch, *J. Am. Chem. Soc.*, **80**, 576 (1958).
(8) I. P. Tsukervanik and Kh. Yu. Yuldashev, *Uzb. Khim. Zh.* 58 (1960); 40 (1961).
(9) I. P. Tsukervanik and Kh. Yu. Yuldashev, *Zh. Obshch. Khim.*, **31**, 858 (1961); **32**, 1293 (1963); **34**, 2647 (1964).
(10) R. M. Roberts and M. B. Abdel-Baset, *J. Org. Chem.*, **41**, 1698 (1976).
(11) J. F. Eykman, *Chem. Weekbl.*, **5**, 655 (1908).
(12) J. B. Niederl, R. A. Smith, and M. E. McGreal, *J. Am. Chem. Soc.*, **53**, 3390 (1931).
(13) A. R. Bader, *J. Am. Chem. Soc.*, **77**, 4155 (1955).
(14) V. V. Korshak, K. K. Samplavskaya, and A. I. Gershanovich, *J. Gen. Chem. USSR (Engl. Transl.)*, **16**, 1065 (1946).
(15) R. Varet and V. J. Vienne, *C. R. Acad. Sci.*, **104**, 1375 (1887).
(16) O. W. Cook and V. J. Chambers, *J. Am. Chem. Soc.*, **43**, 334 (1921).
(17) J. Boeseken and A. A. Adler, *Recl. Trav. Chim. Pays-Bas*, **48**, 474 (1929).
(18) J. S. Reichert and J. A. Nieuwland, *J. Am. Chem. Soc.*, **45**, 3090 (1923); **50**, 2564 (1928).
(19) V. L. Vaiser, *Dokl. Akad. Nauk SSSR*, **70**, 621 (1950); **85**, 85 (1952); **84**, 71 (1952); **87**, 593 (1952).
(20) I. Iwai and T. Hiraoka, *Chem. Pharm. Bull.*, **11**, 638 (1963).
(21) R. C. Petterson, J. T. Bennett, D. C. Lankin, G. W. Lin, J. P. Mykytka, and T. G. Troendle, *J. Org. Chem.*, **39**, 1841 (1974).
(22) I. Iwai and T. Hiraoka, *Chem. Pharm. Bull.*, **14**, 262 (1966).
(23) For reviews and leading references on vinyl cations see L. R. Subramanian and M. Hanack, *J. Chem. Educ.*, **52**, 80 (1975); P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973); G. Modena and U. Tonelato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971); P. J. Stang, M. Hanack, Z. Rappoport, and L. R. Subramanian, "Vinyl Cations", Academic Press, New York, N.Y., in press.
(24) Z. Földi, *Ber.*, **61**, 1609 (1928).
(25) C. D. Nenitzescu et al., *Bull. Soc. Chim. Fr.*, 1272 (1955); *Chem. Ber.*, **90**, 585 (1957); *Tetrahedron*, **19**, 323 (1963).
(26) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957).
(27) W. J. Hickinbottom et al., *J. Chem. Soc.*, 4124 (1957); 1520, 2509, 2517 (1959); 867, 870 (1962); 366, 373, 518 (1963).
(28) G. A. Olah and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 2214 (1974).
(29) C. A. Brown, *J. Org. Chem.*, **39**, 3913 (1974).
(30) P. J. Stang and T. E. Dueber, *Org. Synth.*, **54**, 79 (1974); T. E. Dueber, P. J. Stang, W. D. Pfeifer, R. H. Summerville, M. A. Imhoff, P. v. R. Schleyer, K. Hummel, S. Bocher, C. E. Harding, and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **9**, 521 (1970).
(31) A. G. Anderson and P. J. Stang, *J. Org. Chem.*, **41**, 3034 (1976).
(32) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953).
(33) C. K. Ingold and M. S. Smith, *J. Chem. Soc.*, 905 (1938); P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956); W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).
(34) E. Deutsch and N. K. V. Cheung, *J. Org. Chem.*, **38**, 1123 (1973).
(35) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **88**, 986 (1966).
(36) F. B. Ahrens, *Ber.*, **38**, 155 (1905).
(37) G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.*, **97**, 1845 (1975).
(38) W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *J. Am. Chem. Soc.*, **93**, 1513 (1971).
(39) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).
(40) The linearity of the correlation is improved somewhat (correlation coefficient of 0.999 vs. 0.997) by use of the Yukawa–Tsuno[41] relationship. This results in a $\rho = -2.34$ and an $r = 1.23$; see ref 2 for further details.
(41) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **32**, 971 (1959).
(42) L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963).
(43) C. D. Nenitzescu, S. Titeica, and V. Ioan, *Bull. Soc. Chim. Fr.*, 1272 (1955).
(44) (a) We have found that nitrobenzene cannot be alkylated by vinyl triflates under any conditions just as it cannot be reacted in normal Friedel–Crafts alkylations. (b) C. L. Perrin, *J. Am. Chem. Soc.*, **99**, 5516 (1977).
(45) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4571 (1961).
(46) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **84**, 1688 (1962).
(47) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958); H. S. Klein and A. Streitwieser, Jr., *Chem. Ind. (London)*, 180 (1961).
(48) This also accounts for the relatively low yields of alkylation products in the case of triflates **4** and **5**. Besides alkylation products significant amounts of olefinic products were observed having spectral properties consistent with those of the respective allene dimers.[49] These dimers presumably arose via the allenes derived by proton elimination from the same vinyl cations involved in the alkylation.
(49) G. Wittig and M. Meske-Schuller, *Justus Liebigs Ann. Chem.*, **711**, 55, 76 (1968).
(50) M. Hanack, *Acc. Chem. Res.*, **9**, 364 (1976); Z. Rappoport, *ibid.*, **9**, 265 (1976).
(51) A. Bischler and B. Napieralski, *Ber.*, **26**, 1903 (1893).
(52) W. M. Whaley and T. R. Govindachari, *Org. React.*, **6**, 74 (1951).
(53) H. Decker and W. Kropp, *Ber.*, **42**, 2075 (1909); D. H. Hey and J. M. Williams, *J. Chem. Soc.*, 1527 (1951).
(54) I. Ugi, F. Beck, and V. Fetzer, *Chem. Ber.*, **95**, 125 (1962).
(55) G. Fodor, J. Gal, and B. A. Phillips, *Angew. Chem. Int. Ed. Engl.*, **11**, 919 (1972).
(56) L. Gattermann, *Ber.*, **31**, 1149 (1898); W. E. Truce, *Org. React.*, **9**, 37 (1957).
(57) K. Hoesch, *Ber.*, **48**, 1122 (1915); P. E. Spoerri and A. S. DuBois, *Org. React.*, **5**, 387 (1949).
(58) R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947).
(59) J. W. Williams, Y. J. Dickert, and J. A. Krynitsky, *J. Am. Chem. Soc.*, **63**, 2510 (1941).
(60) H. A. Staab and K. Wendel, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 201.
(61) W. M. Jones and D. D. Maness, *J. Am. Chem. Soc.*, **92**, 457 (1970).

Bromination of Phenylpropiolic Acid and Its Ethyl Ester[1]

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Abstract: The kinetics of the addition of bromine to phenylpropiolic acid, its anion, and its ethyl ester were studied in 75% aqueous acetic acid in the presence of varying amounts of sodium bromide, sodium acetate, and other salts. The reaction of the acid is characterized by the one-term rate equation, $-d[Br_2]_T/dt = k_2[A][Br_2]$, where A is the acetylenic substrate and $[Br_2]_T$ the total titratable bromine. The reaction affords small amounts of *cis*- and *trans*-α,β-dibromocinnamic acids and extensive decarboxylation products, as well as products derived from solvent incorporation. Analysis of the kinetic data and the products suggests that the reaction involves a bimolecular electrophilic attack of bromine on the phenylpropiolate anion and that it proceeds through an open vinyl cation intermediate. The bromination of ethyl phenylpropiolate has an additional third-order term, $k_3[A][Br_2][Br^-]$, which corresponds to a bromide ion catalyzed reaction. The bimolecular term also involves an open vinyl cation intermediate, because both ethyl *cis*- and *trans*-α,β-dibromocinnamates are formed, as well as solvent-incorporated products. By contrast, the termolecular, bromide ion assisted process yields only one product, ethyl *trans*-α,β-dibromocinnamate, and is best represented as an Ad_E-E3 reaction, as has been suggested for other halogenations of acetylenes. The activation paramaters for the reaction of the acid and the ester are consistent with the proposed reaction schemes.

An investigation of the kinetics and the products of the bromination of phenylpropiolic acid ($C_6H_5C{\equiv}CCOOH$), its sodium salt, and its ethyl ester in 75% by volume aqueous acetic acid has been carried out in order to elucidate further the nature of the mechanisms involved in acetylenic halogenation. An earlier study of the kinetics of the bromination of this acid

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