(43) R. G. Zepp and P. J. Wagner, *J. Am. Chem. Soc.*, **92**, 7466 (1970).
(44) N. J. Turro and T. J. Lee, *J. Am. Chem. Soc.*, **92**, 7467 (1970).
(45) N. C. Yang and S. L. Murov, *J. Chem. Phys.*, **45**, 4358 (1966).
(46) The small amount of **24** formed (6%) using acidic methanol can be shown to be due to a competing acid-catalyzed ring opening of lactone **23**. We have no satisfactory explanation to account for the difference in photobehavior of enolates **14** and **27**. Further work is needed before this point can be clarified.
(47) R. Grellmann, J. Palmowski, and G. Quinkert, *Angew. Chem., Int. Ed. Engl.*, **10**, 196, 198, 199 (1971).
(48) G. Quinkert, K. Optiz, W. W. Wiersdorff, and J. Weinlich, *Tetrahedron Lett.*, 1863 (1963).
(49) All melting and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlvev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Carey Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz using a Jeolco-MH-100 spectrometer.
(50) R. D. Kimbrough, Jr., K. W. Kraus, and J. J. Partridge, *J. Org. Chem.*, **30**, 4333 (1965).
(51) R. M. Coates and J. E. Shaw, *J. Org. Chem.*, **35**, 2601 (1970).
(52) A. Padwa and L. Hamilton, *J. Am. Chem. Soc.*, **89**, 102 (1967).
(53) A. Bistrzycki and L. Nowakowsk, *Chem. Ber.*, **34**, 3071 (1901).
(54) M. Busch and R. Knoll, *Chem. Ber.*, **60**, 2243 (1927).
(55) A sample of 3,5-dimethyl-2-hydroxybenzhydrol was obtained by sodium borohydride reduction of 3,5-dimethyl-2-hydroxybenzophenone:[56] mp 102–103°; NMR ($CDCl_3$) τ 7.83 (s, 3 H), 7.80 (s, 3 H), 7.13 (broad s, 1 H), 4.10 (s, 1 H), 3.47 (d, 1 H, J = 2.0 Hz), 3.12 (d, 1 H, J = 2.0 Hz), 2.66 (s, 5 H), 2.37 (s, 1 H); ir (KBr) 3.00, 3.30, 3.41, 6.20, 6.75, 6.90, 7.10, 8.16, 8.67, 9.60, 9.70, 9.90, 10.90, 11.50, 12.00, 12.93, 13.50, and 14.40 μ. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.83; H, 7.13.
(56) K. V. Auwers and W. Mauss, *Chem. Ber.*, **61**, 1504 (1928).
(57) A. C. Smith and W. Wilson, *J. Chem. Soc.*, 1342 (1955).
(58) S. Cohen, *Recl. Trav. Chim. Pays-Bas*, **38**, 118 (1919).
(59) H. F. Ullman, *Ann.*, **291**, 23 (1896).
(60) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 1318 (1970).

Electrophilic Reactions at Multiple Bonds. III.[1a] Addition of Fluorosulfuric Acid to Alkynes. Intermediacy of Open-Chain and Hydrogen-Bridged Vinyl Cations

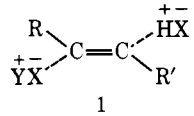
George A. Olah* and Robert J. Spear[1b]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received September 13, 1974*

Abstract: The addition of FSO_3H to a series of alkynes has been studied in SO_2ClF at −120° or SO_2 at −78°. The reactions proceed instantaneously and quantitatively, forming alkenyl (vinyl) fluorosulfates as the primary reaction products. Terminal alkynes, as shown by FSO_3D addition, undergo syn:anti addition in the ratio 4.0:1, the highest ratio yet observed for protic acid addition to such systems. 2-Butyne undergoes predominant anti addition (anti:syn = 6.75:1), while 3-hexyne reacts nonstereospecifically (anti:syn = 9.5:10.0) with FSO_3H, but in the presence of a mole equivalent of pyridinium fluorosulfate it adds anti:syn = 3.0:2.0. 2-Butyne also forms approximately 10% of the 1,2,3,4-tetramethylcyclobutenyl cation, while 1-phenylpropyne forms the 2,4-dimethyl-1,3-diphenylcyclobutenyl cation as the exclusive product. After the initial proton addition, terminal alkynes subsequently react via an open vinyl cation–fluorosulfate ion pair, and aryl-substituted alkynes react by free, open vinyl cations following escape from the ion pair. The data for the addition to 3-hexyne, 2-butyne, and 1,4-dichloro-2-butyne are consistent with the initial formation of hydrogen-bridged vinyl cations which then react competitively via the hydrogen bridge and subsequently formed open vinyl cations.

Electrophilic addition reactions of alkynes have received particular attention during the last decade and have been the subject of several reviews.[2-4] In spite of the volume of experimental data, the mechanistic aspects of these reactions are still not fully understood.[2-4]

The principle question of mechanistic interest concerns the factors which determine the molecularity of the reactions and the nature of the intermediates which are involved. Much of the experimental evidence indicates that bimolecular (AdE2) reactions are occurring via rate-determining addition of the electrophile, although work by Fahey and coworkers[2,5] has suggested that termolecular (AdE3) reactions involving the transition state **1** are important under some conditions. The intermediates from the AdE2 reactions are vinyl cations, which can be either open (**2**) or bridged, i.e., σ bridged (**3**) or π bridged (**4**), the type of bonding being dependent upon the nature of X. Vinyl cations are also intermediates in the solvolysis of vinyl halides, esters, and related systems and have also been extensively reviewed.[2,3,6,7]



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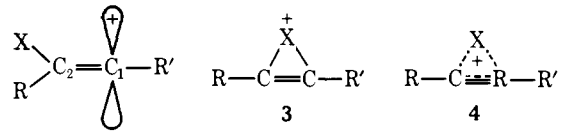


2 3 4

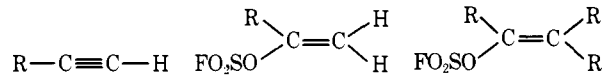
Yates[8] has critically examined the question of open vs. bridged vinyl cations in electrophilic reactions of alkynes and has concluded that "studies of product stereochemistry indicate that phenyl substitution (i.e., R′ = Ph in **2**–**4**) leads to open intermediates (i.e., **2**), except for sulfenyl halide additions, whereas exclusive alkyl substitution (R, R′ = alkyl) leads to bridged ions (**3**, **4**) except for proton addition".[8] Modena and Melloni[9-11] have examined the selectivity of nucleophilic attack on open vinyl cations (i.e., syn or anti to X in **2**) and have demonstrated the expected sensitivity to attack at C_1 due to the size and electronic character of R and X.

The addition of protic acids is the least understood of all the electrophilic reactions of alkynes. Stang[3] has concluded that "the exact behavior and mechanism of electrophilic additions (of acids) to alkynes is clearly strongly dependent upon the reaction conditions. In a highly polar and strongly acidic but weakly nucleophilic solvent such as trifluoroacetic acid, addition via a vinyl cation intermediate is favored

whereas in less polar, more nucleophilic solvents such as acetic acid, a different mechanism prevails." [3]

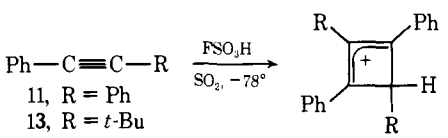
We have chosen to study the reaction of a series of alkynes with fluorosulfuric acid (FSO_3H). This represents the most acidic, least nucleophilic reaction conditions which have so far been studied and clearly rules out participation by AdE3 mechanisms; the formation of distinct ionic intermediates should be strongly favored.

Only a few isolated reactions of alkynes with FSO_3H have been reported. 3-Fluoropropyne (**5**) has been spectroscopically observed to yield 3-fluoro-2-propenyl fluorosulfate (**6**) when treated with FSO_3H in sulfuryl chloride fluoride (SO_2ClF) solution at −20°,[12] while phenylethyne (**7**) gives only polymeric material when reacted with FSO_3H in methylene chloride at −78° but yields 1-phenylethenyl fluorosulfate (**8**) if tri-*n*-propylammonium fluorosulfate is present.[13] Only two other alkenyl (vinyl) fluorosulfates, trifluoroethenyl fluorosulfate (**9**)[14] and triphenylethenyl fluorosulfate (**10**),[13] have been prepared. **9** and **10** are reported to be stable, readily purified compounds,[13,14] while **8** decomposed within a few days,[13] and **6** could not be isolated.[12]



5, R = CH_2F **6**, R = CH_2F **9**, R = F
7, R = Ph **8**, R = Ph **10**, R = Ph

In contrast with the behavior of **5** and **7**, diphenylethyne (**11**) and 3,3-dimethyl-1-phenyl-1-butyne (**13**) give, with FSO_3H in sulfur dioxide (SO_2) solution at −78°, exclusive formation of the cyclobutenyl cations **12** and **14**, respectively.[15a-c]



11, R = Ph
13, R = *t*-Bu

12, R = Ph
14, R = *t*-Bu

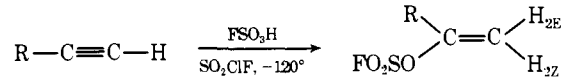
Thus it was of additional interest to investigate the factors which determine the relative proportion of alkenyl fluorosulfates and cyclobutenyl cations, as well as other products which so far have not been detected, in these reactions.

Results

A systematic study of the reaction of FSO_3H with a series of terminal and disubstituted alkynes has been carried out. The standard conditions employed were the addition of the alkyne as an approximately 20% solution in SO_2ClF at −120° to a 1:1 solution of FSO_3H in SO_2ClF at −120°; an approximately 3 mol equiv excess of FSO_3H was used to minimize intermolecular reactions. In some cases, SO_2 at −78° was used as solvent because of limited solubility of the alkyne; full details are described in the Experimental Section. The reactions were followed by ^1H NMR and ^{19}F NMR spectroscopy, and in suitable cases, the stereochemistry of the addition was determined with fluorosulfuric acid-*d* (FSO_3D) addition. Where isomeric products were formed, the isomer ratios were determined from the ^{19}F NMR spectra, except in the deuteration experiments.

The reactions, under these carefully selected conditions, are usually instantaneous and quantitative; no polymer formation can be detected. The ^1H NMR and ^{19}F NMR spectra of the primary reaction products, alkenyl fluorosulfates, and geminal alkylene difluorosulfates, secondary products in some cases, are given in Tables I and II, respectively. Cyclobutenyl cation formation was observed for only two alkynes, and they are described subsequently. It was not possible, however, to fully characterize the alkenyl fluorosulfates by isolation from their solutions, because of decomposition or secondary reactions.

1. Terminal Alkynes. (a) Formation of Alkenyl (Vinyl) Fluorosulfates. Ethyne (**15**) dissolves in SO_2ClF-FSO_3H at

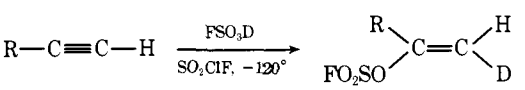


15, R = H
17, R = CH_3
19, R = CH_2CH_3
21, R = $CH_2CH_2CH_2CH_3$
23, R = CH_2Cl
25, R = OCH_2CH_3
27, R = CH_2CH_2OH
28, R = $CH_2CH_2O^+H_2$
30, R = CF_3
31, R = CH=CH_2

16, R = H
18, R = CH_3
20, R = CH_2CH_3
22, R = $CH_2CH_2CH_2CH_3$
24, R = CH_2Cl
26, R = OCH_2CH_3
29, R = $CH_2CH_2O^+H_2$

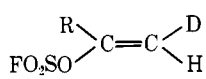
−120° to give a red solution, but no reaction is observed till the temperature is raised to −15° where ethenyl fluorosulfate (**16**) forms slowly. In contrast, propyne (**17**), 1-butyne (**19**), and 1-hexyne (**21**) react instantaneously at −120° to form the fluorosulfates **18, 20,** and **22,** respectively, while under these conditions, it is necessary to heat 3-chloropropyne (**23**) and ethoxyethyne (**25**) to −60° in order that reaction occurs; at this temperature, the appearance of **24** and **26,** respectively, and the disappearance of **23** and **25,** can be observed over 20 min. The reaction of 1-butyn-4-ol (**27**) with FSO_3H in SO_2 at −78° initially yields the O-protonated species **28** [^1H NMR: δ 2.34 (1 H, t, J = 2.8 Hz, ≡CH, 2.78 (2 H, tt, J ≈ 6.0, 2.8 Hz, ≡CCH_2), 4.65 (2 H, t, J = 6.0 Hz, $CH_2O^+H_2$)] which at −40° is slowly converted to **29.** 3,3,3-Trifluoropropyne (**30**) is too deactivated to react even at 0°, while phenylethyne (**7**) and its *p*-methoxy, methyl, and chloro derivatives, as observed previously in CH_2Cl_2 at −78°,[13] and but-3-en-1-yne (**31**) yield only polymeric products.

The stereochemistry of the addition was determined for **17, 19,** and **21** by the use of FSO_3D under identical conditions to that employed for FSO_3H addition; the ratio of (*Z*)-**32**:(*E*)-**32**,[16] (*Z*)-**33**:(*E*)-**33**, and (*Z*)-**34**:(*E*)-**34**, the



17, R = CH_3
19, R = Et
21, R = *n*-Bu

(*Z*)-**32**, R = CH_3
(*Z*)-**33**, R = Et
(*Z*)-**34**, R = *n*-Bu

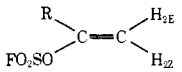
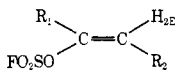
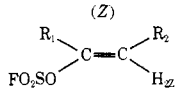


(*E*)-**32**, R = CH_3 Z:E = 4.0:1
(*E*)-**33**, R = Et Z:E = 4.0:1
(*E*)-**34**, R = *n*-Bu Z:E = 4.0:1

respective products, was 4.0:1 in each case and did not alter over an extended period of time. The accidental equivalence of H_{2E} and H_{2Z} in **6, 24,** and **26** (Table I) ruled out such an experiment in these systems, while in the case of ethyne (**15**), H-D exchange is sufficiently rapid at the temperatures necessary for reaction (−15°) that this experiment, and the reverse using ethyne-d_2 with FSO_3H, yielded no conclusive data. The identification of the alkenyl fluorosulfate stereoisomers is discussed in the Appendix.

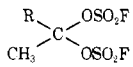
(b) Secondary Reactions. Formation of Geminal Alkylene Difluorosulfates and Isomerizations. When a solution of 2-propenyl fluorosulfate (**18,** formed from **17** at −120°) is warmed to −90°, the vinyl proton resonance gradually dis-

Table I. ^{1}H NMR[a] and ^{19}F NMR[b] Data for the Alkenyl Fluorosulfates

Compd	Chemical shifts[a,b] H_{2Z}	H_{2E}	Additional proton shifts	OSO_2F	Coupling constants[a]
					
16, R = H[c]	5.56	5.36	H_1, 6.95	−35.33	$J_{1,2E} = 6.0; J_{1,2Z} = 13.0; J_{2E,2Z} = 4.2$
18, R = CH_3[d]	5.24	5.18	CH_3, 2.11	−36.38	$J_{2E,2Z} = 4$
20, R = CH_2CH_3[d]	5.23	5.08	CH_2, 2.42; CH_3, 1.15	−36.72	$J_{2E,2Z} = 4.0$
22, R = *n*-Bu[d]	5.27	5.15	CH_2, 2.36, 1.47, 1.47; CH_3, 0.99	−36.11	$J_{2E,2Z} = 4.0$
24, R = CH_2Cl[e]	5.63	5.63	CH_2, 4.36	−39.93	
26, R = OCH_2CH_3[e]	3.82	3.82	CH_2, 4.66; CH_3, 1.54	−33.99	
29, R = $CH_2CH_2O^+H_2$[g]	5.53	5.40	CH_2, 4.70, 2.97	−37.15	$J_{2E,2Z} = 4.5; J_{2Z,F} = 1.8; J_{2E,F} = 0.8$
6, R = CH_2F[f,i]	5.80	5.80	CH_2, 4.16	−37.73	
8, R = Ph[h]	5.37	5.55	Ph, 7.35		$J_{2E,2Z} = 3.5; J_{2Z,F} = 1.0$
 (*Z*)					
 (*E*)					
(*Z*)-**39**, $R_1 = R_2 = CH_3$[f]		5.59	C_1–CH_3, 2.24; C_2–CH_3, 1.88	−39.93	$J_{2E,C_2-CH_3} = 7.2$
(*E*)-**39**, $R_1 = R_2 = CH_3$[f]	5.93		C_1–CH_3, 2.24; C_2–CH_3, 1.88	−35.60	$J_{2Z,C_2-CH_3} = 7.2$
(*Z*)-**40**, $R_1 = CH_3$; R_2 = *n*-Pr[f]		5.35	CH_2, 2.10, 1.45; CH_3, 2.10, 0.95	−40.15	$J_{2E,C_2-CH_2} = 7.5$
(*E*)-**40**, $R_1 = CH_3$; R_2 = *n*-Pr	5.70		CH_2, 2.10, 1.45; CH_3, 2.10, 0.95	−36.03	$J_{2Z,C_2-CH_2} = 8.0; J_{2Z,F} = 1$
(*Z*)-**45**, $R_1 = R_2 = CH_2CH_3$[f]		5.49	CH_2, 2.2–2.8 (m); CH_3, 1.29, 1.19	−40.04	$J_{2E,C_2-CH_3} = 7.0; J_{2E,F} = 0.8$
(*E*)-**45**, $R_1 = R_2 = CH_2CH_3$[f]	5.82		CH_2, 2.2–2.8 (m); CH_3, 1.29, 1.19	−36.56	$J_{2Z,C_2-CH_3} = 8.0; J_{2Z,F} = 2.0$
(*Z*)-**47**, $R_1 = R_2 = CH_2Cl$[j]		6.29	C_1–CH_2, 4.59; C_2–CH_2, 4.41	−41.06	$J_{2E,C_2-CH_3} = 8.0$
(*E*)-**47**, $R_1 = R_2 = CH_2Cl$[j]	6.44		C_1–CH_2, 4.63; C_2–CH_2, 4.41	−39.33	$J_{2Z,C_2-CH_3} = 8.0$
(*E*)-**53**, R_1 = H; $R_2 = C^+(OH)_2$[j]	6.74		H_1, 8.69	−42.85	$J_{1,2Z} = 12.0$
(*E*)-**56**, $R_1 = CH_3$; $R_2 = C^+(OH)_2$[j]	6.65		CH_3, 2.85	−43.06	
(*Z*)-**56**, $R_1 = CH_3$; $R_2 = C^+(OH)_2$[j]		6.25	CH_3, 2.73	−46.60	
(*E*)-**59**, R_1 = Ph; $R_2 = C^+(OH)_2$[g]	6.54		Ph, 7.5–7.7 (m)	−45.02	

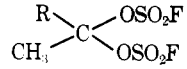
[a] Proton chemical shifts are in parts per million from internal (capillary) Me_4Si. Coupling constants are in hertz. [b] Fluorine chemical shifts are in parts per million from internal (capillary) $CFCl_3$; negative sign signifies downfield. [c–f] In FSO_3H–SO_2ClF at −15, −105, −20, and −50°, respectively. [g] In FSO_3H–SO_2 at −15°. [h] In CCl_4 at room temperature, data from ref 13. [i] Data from ref 12. [j] In FSO_3H at 30°.

Table II. ^{1}H NMR[a] and ^{19}F NMR[b] Data for the Geminal Alkylene Difluorosulfates

Compd	CH_3	R	OSO_2F
			
35, R = H[c]	2.05, d, J = 6.0	7.02, q, J = 6.0	−42.04
36, R = CH_3[d]	2.12	2.12	−45.90
37, R = CH_2CH_3[d]	2.12	CH_2, 2.42, q, J = 7.5; CH_3, 1.15, t, J = 7.5	−46.67
38, R = $CH_2CH_2CH_2CH_3$[d]	2.10	*e*	−46.07

[a] Proton chemical shifts are in parts per million from internal (capillary) Me_4Si; coupling constants are in hertz. [b] Fluorine chemical shifts are in parts per million from internal (capillary) $CFCl_3$; the negative sign signifies downfield. [c,d] In FSO_3H–SO_2ClF at −15 and −80°, respectively. [e] Signals obscured by those of **22** (Table I).

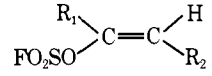
appears, and the methyl resonance becomes enhanced. Concurrently, the ^{19}F resonance of **18** (−36.38) is replaced by a new signal at ϕ − 45.90, downfield of the FSO_3H resonance (−41.0), and these changes indicate that **18** has added a second mole of FSO_3H to give propane 2,2-difluorosulfate (**36**, Table II). As the temperature is raised further, the ^{19}F resonance of **36** and the excess FSO_3H broaden at −80° and coalesce into a single broad resonance at −30°, indicating fast fluorosulfate exchange under these conditions. Further increase of temperature to −20° results in decomposition.



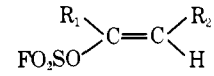
35, R = H
36, R = CH_3
37, R = CH_2CH_3
38, R = $CH_2CH_2CH_2CH_3$

The reactions of 1-butyne (**19**) and 1-hexyne (**21**) with FSO_3H follow a similar pattern via **20** and **22** and then slow formation of **37** and **38**, respectively (Table II) at −70°. However, before complete conversion to **37** and **38** and significant broadening of the ^{19}F resonance occurs (cf. **36**, above), isomerization to (*Z*)-**39** and (*E*)-**39**,[16] ratio 4.75:1, and (*Z*)-**40** and (*E*)-**40**, ratio 3.5:1, respectively, takes place. When **19** is reacted with FSO_3D [forming (*Z*)-**33** and (*E*)-**33** in the ratio 4.0:1, as discussed previously] and is warmed to −40°, isomerization occurs to (*E*)-**41** and (*Z*)-**41**; the incorporation of a second deuterium into the C_1–CH_3 in only 50% of the molecules indicates a significant kinetic isotope effect. Ethenyl fluorosulfate (**16**) which forms at −15°, slowly adds a second molecule of FSO_3H at this temperature to give **35** (Table II). **24**, **26**, and **29** do not add a second mole of FSO_3H at accessible temperatures.

2. Disubstituted Alkynes and Alkynoic Acids. 2-Butyne (**42**) reacts instantaneously with FSO_3H in SO_2ClF at

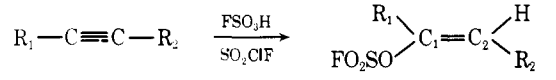


(*Z*)-**39**, $R_1 = R_2 = CH_3$
(*Z*)-**40**, $R_1 = CH_3$; $R_2 = CH_2CH_2CH_3$
(*Z*)-**41**, $R_1 = CH_{1.5}D_{1.5}$; $R_2 = CH_3$



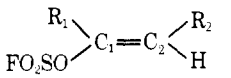
(*E*)-**39**, $R_1 = R_2 = CH_3$
(*E*)-**40**, $R_1 = CH_3$; $R_2 = CH_2CH_2CH_3$
(*E*)-**41**, $R_1 = CH_{1.5}D_{1.5}$; $R_2 = CH_3$

−120°, forming (*Z*)-**39**, (*E*)-**39** (Table I), and the 1,2,3,4-tetramethylcyclobutenyl cation (**43**, ^1H NMR spectrum identical with that reported for this ion generated from 3-chloro-1,2,3,4-tetramethylcyclobut-1-ene and $AlCl_3$ in CH_2Cl_2)[17] in the ratio 6.75:1.1. The reaction mixture can

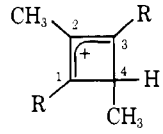


42, $R_1 = R_2 = CH_3$
44, $R_1 = R_2 = CH_2CH_3$
46, $R_1 = R_2 = CH_2Cl$
48, $R_1 = R_2 = CF_3$
49, $R_1 = Ph$; $R_2 = CH_3$

(*Z*)-**39**, $R_1 = R_2 = CH_3$
(*Z*)-**45**, $R_1 = R_2 = CH_2CH_3$
(*Z*)-**47**, $R_1 = R_2 = CH_2Cl$



(*E*)-**39**, $R_1 = R_2 = CH_3$
(*E*)-**45**, $R_1 = R_2 = CH_2CH_3$
(*E*)-**47**, $R_1 = R_2 = CH_2Cl$



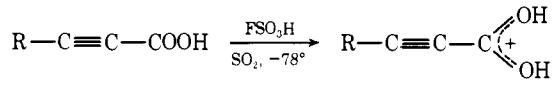
43, R = CH_3
50, R = Ph

be warmed to −20° without change. Repetition of the reaction using FSO_3D removed only the signals corresponding to H_2 in (*Z*)-**39** and (*E*)-**39** and H_4 in **43** (and the couplings associated therewith); no deuterium was incorporated into other positions even after extended periods at −40°. 3-Hexyne (**44**) reacts under identical conditions to give (*Z*)-**45** and (*E*)-**45**, ratio 9.5:10.0; no cyclobutenyl cations (or other products) were detected. In the presence of a mole equivalent (with respect to **44**) of pyridinium fluorosulfate, **44** reacts with FSO_3H in SO_2ClF at −78° to give (*Z*)-**45** and (*E*)-**45**, ratio 3.0:2.0.

In contrast, 1-phenylpropyne (**49**) reacts with FSO_3H in SO_2ClF at −120° (or −78°) to give exclusive formation of the cyclobutenyl cation **50** [^1H NMR: δ 1.47 (3 H, d, J_{H_4,CH_3} = 6.9 Hz, C_4-CH_3), 2.42 (3 H, d, J_{H_4,CH_3} = 2.3 Hz, C_2-CH_3), 4.40 (1 H, broad m, H_4), 8.04, 7.61, 7.80 (total 5 H, H_{ortho}, H_{meta}, H_{para},), respectively], although polymer formation (broad ^1H NMR absorption, δ 6.6-7.4) accounts for approximately 30% of **49** consumed.

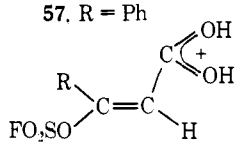
As observed in the terminal alkynes, halogen substitution lowers the reactivity, and 1,4-dichloro-2-butyne (**46**) and hexafluoro-2-butyne (**48**) will not react, in SO_2ClF, even at 0°. **46** reacts, however, in neat FSO_3H at 0° to give (*Z*)-**47** and (*E*)-**47**, ratio 5.0:1 (Table I); the low-boiling point of **48** did not permit a similar experiment.

Propynoic acid (**51**), 2-butynoic acid (**54**), and phenylpropynoic acid (**57**) all quantitatively protonate in FSO_3H-SO_2 at −78°, forming **52**, **55**, and **58**, respectively (^1H NMR: **52**, δ_{CH} = 4.20; **55**, δ_{CH_3} = 2.14; **58**, $\delta_{H_{ortho}}$, $\delta_{H_{meta}}$, $\delta_{H_{para}}$ = 7.80, 7.46, 7.62, respectively). Upon warming these solutions to −15°, **58** slowly yields (*E*)-**59**[16] (Table I), but **53** and **56** do not react further. However, **51** reacts in neat FSO_3H at 20° to form (*E*)-**53**, while **54**, under the same conditions, yields (*E*)-**56** and (*Z*)-**56**, ratio 5.5:1. The identification of the alkenyl fluorosulfate stereoisomers is described in the Appendix.

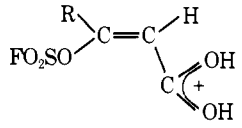


51, R = H
54, R = CH_3
57, R = Ph

52, R = H
55, R = CH_3
58, R = Ph



(*E*)-**53**, R = H
(*E*)-**56**, R = CH_3
(*E*)-**59**, R = Ph

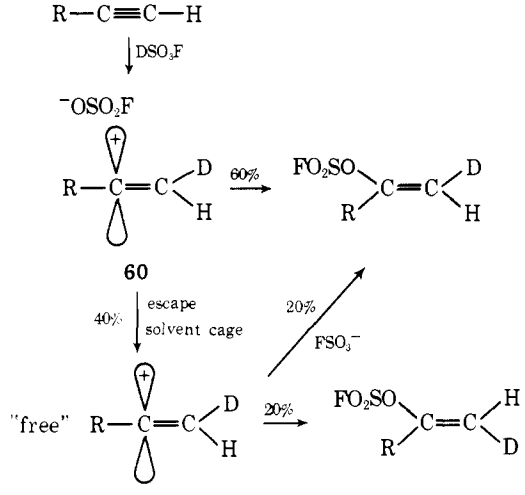


(*Z*)-**56**, R = CH_3

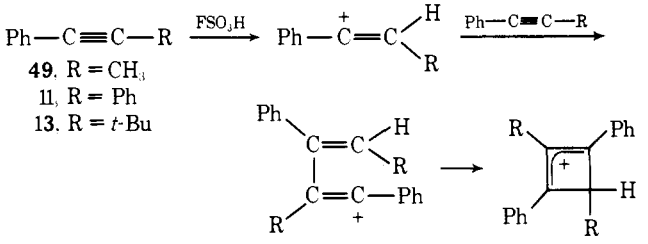
Discussion

Electrophilic protic acid addition to alkynes can follow either AdE2 or AdE3 mechanisms.[2-5] Typically, under conditions of low reactivity, such as HCl in HOAc, alkynes having exclusive alkyl substitution (e.g., 3-hexyne)[5] react by AdE3 mechanisms with predominant anti addition, while aryl-substituted alkynes (e.g., 1-phenylpropyne),[2] under the same conditions, follow AdE2 mechanisms and react via a tight ion pair leading to predominant syn addition. Peterson[18] has studied the reaction of 3-hexyne with trifluoroacetic acid, a more reactive electrophile; the formation of (*E*)- and (*Z*)-3-hexenyl trifluoroacetates in approximately equal amounts, together with a small amount of hexaethylbenzene, is regarded as the strongest evidence for vinyl cations in electrophilic additions to alkynes.[2-4] Schleyer has recently extended the study of trifluoroacetic acid addition to alkynes.[19]

Earlier results[2-4] for protic acid addition to terminal alkynes indicated predominant anti addition, but recently it has been shown, by deuterium labeling, that HCl reacts with phenylethyne[9] and 1-hexyne[5] to yield both syn and anti addition in the ratio 6:4. It has also been noted that 1-hexyne undergoes 74% syn addition of trifluoromethanesulfonic acid (CF_3SO_3H).[19] The results obtained in our present work for the addition of FSO_3H to propyne, 1-butyne, and 1-hexyne represent the highest syn:anti ratios yet observed for acid addition to terminal alkynes (4.0:1). The deuteration experiments clearly demonstrate the irreversibility of the reactions and rule out acid-catalyzed isomerization by excess acid. The evidence can be readily interpreted mechanistically as initial protonation of the alkyne to form an open vinyl cation -FSO_3^- ion pair (**60**) which subsequently collapses to syn product in 60% of cases, while 40% of the vinyl cations escapes the solvent cage to give "free"[20] open vinyl cations which undergo nonstereospecific nucleophilic attack giving statistical syn and anti addition (see following scheme). Alternatively, the 20% anti ad-



dition could originate from external attack on the initially formed ion pair (**60**). In contrast, disubstituted alkynes appear to react through free[20] vinyl cations. The formation of cyclobutenyl cations from 1-phenylpropyne (**49**), diphenylethyne (**11**),[15a-c] and 3,3-dimethyl-1-phenyl-1-butyne (**13**)[15a-c] clearly involves free open vinyl cations which react with a second molecule of alkyne (supporting the assumption that protonation is the slow step in the addition reactions) and subsequently cyclize to **50, 12,** and **14,** respectively. It seems likely that the polymerization of phenylethyne, and the partial polymerization of **49,** is due to intermolecular processes competing with the intramolecular cyclization step.

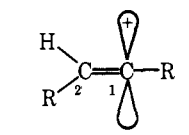


49, R = CH_3
11, R = Ph
13, R = *t*-Bu

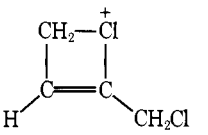
50, R = CH_3
12, R = Ph
14, R = *t*-Bu

The alkenyl fluorosulfate isomer distributions observed in this work for the addition of FSO_3H to 2-butyne (**42**) and 3-hexyne (**44**) are similar to the data reported for trifluoroacetic acid[18,19] addition. In the presence of a mole equivalent (with respect to **44**) of pyridinium fluorosulfate, **44** yields anti:syn addition in the ratio 3.0:2.0. 1,4-Dichloro-2-butyne (**46**), as **42,** gives predominant anti addition; the complete isomer distributions for **42, 44,** and **46** are shown below. **42** has been reported to add CF_3SO_3H in the ratio syn (**35**):anti (**65**).[21]

Free[20] open vinyl cations with equivalent groups at C-2 (i.e., **2**, R = X) will give statistical syn and anti addition. In the case of **42, 44,** and **46,** the intermediate vinyl cation (**61**), by analogy with the results of Modena and Melloni[9-11] should slightly favor syn addition because of the lessened steric hindrance to nucleophilic attack syn to H. Indeed, the slightly greater proportion of (*E*)-**45** (10.0) to (*Z*)-**45** (9.5) from **44** supports this assumption. However, the preferred anti addition to **42, 46,** and to **44** in the presence of pyridinium fluorosulfate (i.e., more nucleophilic conditions) cannot be explained by such phenomena. The participation of AdE3 mechanisms, which would give anti addition, can, as discussed in the introductory section, be ruled out under these conditions. A cyclic chloronium ion intermediate (**62**) could be envisaged from **46;** although such intermediates have been postulated from vinyl cations



61
R = CH_3, Et, CH_2Cl, *n*-Pr



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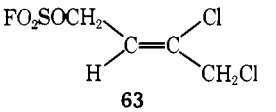
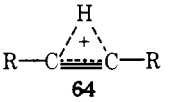


63

involving five-membered ring chloronium ions,[18,22] it would be expected that a four-membered ring (as in **62**) would form with extreme difficulty, and the absence of any rearranged products (**63**) rules out participation of this intermediate.

The formation of the cyclobutenyl cation **43,** as a minor product from **42,** clearly shows that free[20] open vinyl cations are present, to some extent, as intermediates in this reaction. We propose that the anti addition to **42** and **46** is due to nucleophilic attack on the intermediate hydrogen-bridged vinyl cations (**64** or **65**).[23] In the case of **44,** the isomer distribution indicates that nucleophilic attack is occurring on the open vinyl cation which has formed by subsequent collapse of the hydrogen-bridged vinyl cation. Evidence supporting this view can be seen in the preferred anti addition of FSO_3H to **44** in the presence of pyridinium fluorosulfate; under these more nucleophilic conditions, some attack can occur on the hydrogen-bridged vinyl cation prior to formation of the open ion. Alternatively, the increased anti addition could be due to external attack on the initially formed ion pair. Recent ab initio calculations have predicted that the bridged form is energetically more favorable for the parent vinyl cation,[24] while the open forms are energetically favored in substituted vinyl cations.[25]



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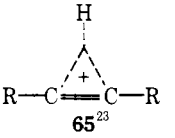
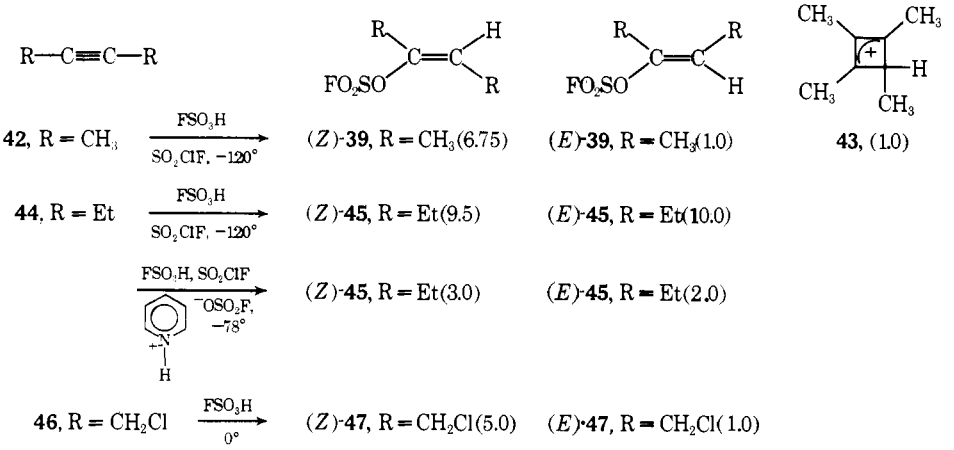


65[23]

An alternative explanation for the stereochemistry of addition has been proposed by Schleyer[19] who interpreted the results for trifluoroacetic acid addition to **42, 44,** and 4-octyne as involving free, open vinyl cations (**61**). The predominance of anti addition to **42** was explained by an attractive effect of the β-methyl group, rendered electron deficient by hyperconjugation, and the attacking nucleophile.[19] However, it is difficult to see that this attractive effect should be sufficiently different in **61,** R = CH_3, CH_2CH_3, CH_2Cl, and *n*-Pr, to produce such diverse results. Although the



42, R = CH_3 — FSO_3H, SO_2ClF, −120° → (*Z*)-**39**, R = CH_3 (6.75); (*E*)-**39**, R = CH_3 (1.0); **43**, (1.0)

44, R = Et — FSO_3H, SO_2ClF, −120° → (*Z*)-**45**, R = Et (9.5); (*E*)-**45**, R = Et (10.0)

FSO_3H, SO_2ClF, $^-OSO_2F$, −78° → (*Z*)-**45**, R = Et (3.0); (*E*)-**45**, R = Et (2.0)

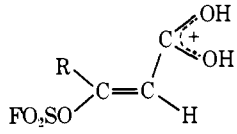
46, R = CH_2Cl — FSO_3H, 0° → (*Z*)-**47**, R = CH_2Cl (5.0); (*E*)-**47**, R = CH_2Cl (1.0)

probability of external attack occurring on the ion pair is considered to be low under our experimental conditions (in highly ionizing FSO_3H-SO_2 or FSO_3H-SO_2ClF solutions), it does offer an alternative explanation to be kept in mind. However, if one is to invoke steric hindrance to external attack on the ion-pair intermediate corresponding to **61,** this cannot explain the similarity for the results from R = CH_3 and R = CH_2Cl, in contrast to R = CH_2CH_3.

A further difficulty for such an explanation is that 3-hexyne (**44**) (and 4-octyne with CF_3COOH) gives results typical of free[20] open vinyl cations subsequently undergoing nucleophilic attack. It is difficult to see why propyne (**17**) and 1-butyne (**19**) should react by ion-pair collapse; 2-butyne (**42**) undergoes substantial external attack by FSO_3H on the initially formed ion pair, while **44** gives free open vinyl cations, when the differences in the stability of these ions should be comparatively small.

We suggest that the intermediate ions from **42** and **44** escape the ion pair, because they are initially hydrogen bridged and hence cannot undergo syn attack. The differing subsequent behavior, i.e., **44,** reacts exclusively via an open ion, while **42** reacts predominantly via the hydrogen-bridged ion, is most likely due to differing relative stabilities (i.e., energy difference between the open and hydrogen-bridged ions in the two cases), but one cannot rule out differing reactivities of the hydrogen-bridged ions. The intermediacy of bridged vinyl cations in sulfenyl halide[2,4,8,26] and bromine addition[2-4,8] to alkynes is firmly established.

The apparent syn addition to propynoic acid (**51**), 2-butynoic acid (**54**), and phenylpropynoic acid (**57**) to yield (*E*)-**53,** (*E*)-**56,** and (*E*)-**59,** respectively, is due to subsequent isomerization of the initially formed products, thereby minimizing the electronic repulsions. Similar isomerizations have been observed previously.[27]



(*E*)-**53**, R = H
(*E*)-**56**, R = CH_3
(*E*)-**59**, R = Ph

Conclusions

Terminal alkynes react with FSO_3H to initially form a solvent-separated open vinyl cation -FSO_3^- ion pair which collapses, giving predominant syn addition. The vinyl cations formed from aryl-substituted alkynes, possessing greater stability due to charge delocalization, escape the ion pair, react with a second molecule of alkyne, and subsequently cyclize to cyclobutenyl cations. The data for the addition of FSO_3H to 2-butyne, 3-hexyne, and 1,4-dichloro-2-butyne are most consistent with the initial formation of hydrogen-bridged vinyl cations which escape the ion pair and subsequently react as free[20] vinyl cations. The hydrogen-bridged vinyl cation from 3-hexyne appears to collapse to the open vinyl cation prior to nucleophilic attack, while 2-butyne and 1,4-dichloro-2-butyne react predominantly via the hydrogen-bridged ion. Whether this is due to greater reactivity of the bridged ion in the latter cases, or greater instability of the bridged ion in the former case cannot at this point be determined. In the case of alkynes where the two attached groups are not equal, i.e., terminal alkynes and monophenyl alkynes, if hydrogen-bridged ions are initially formed, they are so highly polarized as to not represent discrete intermediates, rapidly collapsing to open vinyl cations.

The present study extends our general concepts of electrophilic interactions with π systems[28a] from alkenes[28b] and aromatic systems[28c] to alkynes, showing that in each case, the initial interaction involves π-bridged species which then can open to the corresponding carbenium ions.

Experimental Section

The alkynes studied in this work were all commercial samples of the highest purity. Fluorosulfuric acid was refluxed under a stream of nitrogen and freshly distilled prior to use. Fluorosulfuric acid-*d* (Cationics) had an isotopic purity >99.9%; there was no detectable resonance in the ^1H NMR spectrum. Ethyne-d_2 was generated by the addition of deuterium oxide to calcium carbide.

Reactions of the Alkynes with Fluorosulfuric Acid. (a) In SO_2ClF or SO_2. An approximately 20% solution of the alkyne in SO_2ClF at −120° (ethanol–liquid nitrogen slush) or SO_2 at −78° (acetone–Dry Ice slurry) was added dropwise, with rapid shaking and cooling, to a 1:1 solution of FSO_3H in SO_2ClF at −120° or SO_2 at −78°. The resulting solution was transferred to an NMR tube at −120 or −78°, respectively, and the reaction was studied by ^1H NMR and ^{19}F NMR spectroscopy, while the temperature was varied in the range −110 to −10° (SO_2ClF) or −78 to −15° (SO_2). Except in the few examples discussed in the Results section, the reactions were instantaneous. In all cases, an approximately 3 *M* excess (with respect to the alkyne) of FSO_3H was used.

The reaction of 3-hexyne with FSO_3H–pyridinium fluorosulfate was achieved by the initial addition of 1 mol equiv of pyridine (with respect to 3-hexyne) to a 1:1 solution of excess FSO_3H in SO_2ClF at −78°. The resulting mixture was shaken rapidly to afford complete dissolution, then the 3-hexyne was reacted at −78° as described above.

(b) In Neat FSO_3H. The alkyne was cooled to −78° and then was added, in small portions, to a rapidly shaken sample of FSO_3H cooled to −78°. The resulting solutions were studied as above.

Proton and Fluorine Magnetic Resonance Spectra. ^1H NMR and ^{19}F NMR spectra were obtained with a Varian Associates Model A56/60A spectrometer equipped with a variable-temperature probe. External Me_4Si (capillary) and $CFCl_3$ (capillary) were used as a reference for ^1H NMR and ^{19}F NMR spectra, respectively.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged. We also thank Professor P. v. R. Schleyer for stimulating discussions.

Appendix. Stereochemical Assignments

The assignment of proton resonances in olefins is often relatively simple since the substituent shielding effects (additivity effects) of an extremely large number of substituents have been tabulated.[29,30] The assignments of H_1, H_{2E}, and H_{2Z} in ethenyl fluorosulfate (**16,** Table I) are straightforward because of the characteristic vinylic coupling constants; H_{2Z}, the proton cis to the fluorosulfate group, is deshielded relative to H_{2E} with $\Delta\delta_{H_{2E}-H_{2Z}}$ 0.20 ppm.

The assignment of H_{2E} and H_{2Z} in the terminal alkenyl fluorosulfates follow from the result for **16** and application of the additivity rules.[29,30] In all cases except **8,** because of the usual deshielding of the proton cis to the phenyl group (H_{2E}), and **24, 26,** and **6,** where H_{2E} and H_{2Z} are accidentally equivalent, H_{2Z} is deshielded relative to H_{2E}. The assignment in the deuteration (FSO_3D) experiments follow by analogy.

The disubstituted alkenyl fluorosulfates were, by analogy, assigned by the preferential deshielding of H_{2Z} in the E isomers, relative to H_{2E} in the Z isomers, by the fluorosulfate group (Table I). Additional evidence can be seen in the ^{19}F chemical shifts; in the E isomers (*E*)-**39,** (*E*)-**40,** (*E*)-**45,** and (*E*)-**47,** the fluorosulfate resonance is very similar to the terminal analogs **18, 20, 22,** and **24,** while that in the Z isomers, where the group at C_2 is cis to the fluorosulfate group, is substantially deshielded. The assignments of (*E*)-**56** and (*Z*)-**56** follow by analogy, and (*E*)-**53** and (*E*)-**59,**

the only isomers formed, are assigned because of the similarity of the ^{19}F chemical shifts to (*E*)-**56**.

References and Notes

(1) (a) Part II: G. A. Olah, P. Schilling, P. W. Westerman, and H. C. Lin, *J. Am. Chem. Soc.*, **96**, 3581 (1974). (b) Postdoctoral research associate.
(2) R. C. Fahey in "Topics in Stereochemistry", Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience, New York, N.Y., 1968, p. 237.
(3) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971).
(4) P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 276 (1973).
(5) R. C. Fahey, M. T. Payne, and D-J. Lee, *J. Org. Chem.*, **39**, 1124 (1974), and references therein.
(6) H. G. Richey, Jr., and J. M. Richey in "Carbonium Ions", Vol. 2, G. A.Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1970.
(7) M. Hanack, *Acc. Chem. Res.*, **3**, 209 (1970).
(8) K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H-W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, **95**, 160 (1973), and references therein.
(9) F. Marcuzzi, G. Melloni, and G. Modena, *Tetrahedron Lett.*, 413 (1974).
(10) R. Maroni, G. Melloni, and G. Modena, *J. Chem. Soc., Chem. Commun.*, 857 (1972).
(11) R. Maroni, G. Melloni, and G. Modena, *J. Chem. Soc., Perkin Trans. 1*, 353 (1974), and references therein.
(12) G. A. Olah, J. Nishimura, and Y. K. Mo, *Synthesis*, 661 (1973).
(13) W. M. Jones and D. D. Maness, *J. Am. Chem. Soc.*, **92**, 5457 (1970).
(14) M. A. Belaventsev, G. A. Sokol'skii, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2461 (1967).
(15) (a) A. E. Lodder, H. M. Buck, and L. J. Oosterhoff, *Recl. Trav. Chim. Pays-Bas*, **89**, 1229 (1970); (b) A. E. van der Hout-Lodder, H. M. Buck, and J. W. de Haan, *ibid.*, **91**, 164 (1972); (c) A. E. van der Hout-Lodder, H. M. Buck, J. W. de Haan, and L. J. M. van de Ven, *ibid.*, **92**, 1040 (1973).
(16) For the definition of the E-Z nomenclature, see J. E. Blackwood, C. F. Gladys, K. L. Loening, A. E. Petrarca, and J. A. Rush, *J. Am. Chem. Soc.*, **90**, 509 (1968).
(17) T. J. Katz and E. H. Gold, *J. Am. Chem. Soc.*, **86**, 1600 (1964).
(18) (a) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **85**, 2865 (1963); (b) *ibid.*, **88**, 4990 (1966).
(19) R. H. Summerville and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 1110 (1974).
(20) A cation formed by protonation in solution is obviously associated, in some way, with an anion. We use "free" here to denote a vinyl cation which has escaped the ion pair which initially forms upon protonation of the alkyne.
(21) P. J. Stang and R. H. Summerville, *J. Am. Chem. Soc.*, **91**, 4600 (1969).
(22) I. L. Reich and H. J. Reich, *J. Am. Chem. Soc.*, **96**, 2654 (1974).
(23) For simplicity, the three-centered bonds in **65** are depicted by triangular dotted lines drawn from and meeting each other between the three participating atoms: G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973).
(24) B. Zurawski, R. Alrichs, and W. Kutzelnigg, *Chem. Phys. Lett.*, **21**, 309 (1973).
(25) L. Radom, P. C. Hanrihan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 6531 (1973), and references cited therein.
(26) T. Okuyama, K. Izawa, and T. Fueno, *J. Org. Chem.*, **39**, 351 (1974), and references therein.
(27) F. Montanari, *Tetrahedron Lett.*, 518 (1968).
(28) (a) G. A. Olah, "Carbocations and Electrophilic Reactions", Wiley, New York, N.Y., 1973; (b) G. A. Olah and T. R. Hockwender, Jr., *J. Am. Chem. Soc.*, **96**, 3574 (1974); (c) G. A. Olah, *Acc. Chem. Res.*, **4**, 171 (1971), and references cited therein.
(29) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy", 2nd Ed., Pergamon, London, 1969, Chapter 3-3.
(30) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

Nucleophilic Heteroaromatic Substitutions. XXXVIII.[1] Evidence for a Cyclic Mechanism in the Reaction of 2-Phenoxy-1,3,5-triazine with Piperidine in Isooctane

Gabriello Illuminati,* Francesco La Torre, Giancarlo Liggieri, Giancarlo Sleiter, and Franco Stegel

Contribution from the Centro del Consiglio Nazionale delle Ricerche dei Meccanismi di Reazione, Istituto Chimico dell'Università, I-00100 Roma, Italy.

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Abstract: The kinetics of piperidino dephenoxylation of 2-phenoxy-1,3,5-triazine in isooctane have been followed spectrophotometrically. The reaction follows third-order kinetics, is not base-catalyzed, is moderately speeded up by added 2-piperidone, and proceeds by a temperature-independent rate in the range 20-70°. A sizable direct kinetic hydrogen isotope effect is observed, when piperidine-*1-d* is used, that was found to decrease as the concentration of piperidine is increased. Out of several reaction paths, the results support a cyclic mechanism involving the participation of a second molecule of piperidine acting as a bifunctional catalyst.

Much physical organic research in the field of nucleophilic substitution of nitro-activated aromatic compounds has been concerned with kinetic studies involving protic amines as nucleophiles. As reviewed recently,[2] base-catalysis studies have given valuable information about the role of tetrahedral intermediates in aromatic substitution.

In the field of aza-activated heteroaromatic substitution, extensive kinetic work has provided a quantitative evaluation of the role of the heteroatom and revealed such special-reaction features as solvent effects and acid catalysis.[3] However, little effort has been devoted to the investigation of details of the mechanism through the study of base catalysis.[4]

We now wish to report on the kinetic behavior of the reaction of 2-phenoxy-1,3,5-triazine with piperidine in isooctane (2,2,4-trimethylpentane).

A nonpolar solvent was chosen in order to minimize specific effects of the solvent upon the course of the reaction. The reaction involves the nucleophilic displacement of a fairly good leaving group from a substrate where activation is exclusively provided by the aza groups. Kinetic studies of nucleophilic substitution on monosubstituted triazine derivatives had not been reported previously; the choice of a monosubstituted triazine was intended to avoid conjugative interactions of the ring nitrogens with substituents other than the outgoing phenoxy group. We have found that, out of the reactions of several monosubstituted triazine derivatives with piperidine in a nonpolar, aprotic solvent, only that of the phenoxy derivative turned out hitherto well suited for kinetic measurements.

Experimental Section

Melting points and boiling points are uncorrected. Microanalysis was performed by "A. Bernhardt" Mikroanalytisches Laboratorium—Elbach über Engelskirchen (F.G.R.).

2-Phenoxy-1,3,5-triazine was prepared from 2,4,6-trichloro-1,3,5-triazine as described by Hirt et al.[5] and was purified by vacuum distillation and recrystallization from petroleum ether (bp