Stereoselectivity and Mechanisms of Acid-Catalyzed Additions of Acetic Acid to (E)- and (Z)-2-Butene in Acetic Acid[1]

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Abstract: The stereoselectivity and mechanisms of acid-catalyzed additions of acetic acid to (*E*)- and (*Z*)-2-butene in acetic acid have been studied. With the weak acid catalysts deuterium chloride, deuterium bromide, and methanesulfonic acid-*O-d* in acetic acid-*O-d*, the additions proceeded 84 ± 2% anti with no alkene diastereomerization or positional isomerization, or hydrogen–deuterium exchange with solvent. These reactions are proposed to proceed via concerted AdE3 processes. In contrast, with the very strong acid trifluoromethanesulfonic acid-*O-d* in acetic acid-*O-d*, lower stereoselectivity, alkene diastereomerization and positional isomerization, and hydrogen–deuterium exchange are observed. This reaction is proposed to proceed via an AdE2 pathway involving reversible formation of a tight-ion pair, or free carbenium ion.

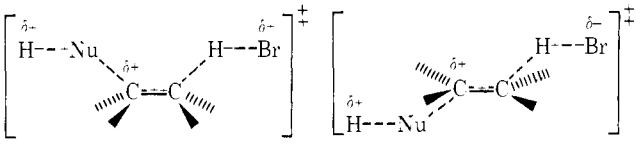
Introduction

Previous investigations in our laboratories have been devoted to the study of the mechanism of the addition of hydrogen bromide, and the hydrogen bromide catalyzed addition of acetic acid, to the (*E*)- and (*Z*)-2-butenes and -3-hexenes, and cyclopentene.[2] Kinetic studies showed that alkyl bromide and alkyl acetate were formed according to the rate expressions

$$\frac{d[RBr]}{dt} = k[HBr]^2[alkene] \quad (1)$$

$$\frac{d[ROAc]}{dt} = k[HBr][alkene] \quad (2)$$

respectively. The lack of an acidity function correlation with rate of reaction[3] and less than unity H–D (k_H/k_D) isotope effects dictated that proton, or deuteron, is delivered by undissociated HBr, or DBr. The lack of H–D exchange in unreacted alkene, alkene isomerization (both positional and diastereomerization), and hydride shift rearrangement products in the 3-hexene system militated against formation of a tight-ion pair or free carbenium ion. The stereochemistry of the addition of *both* DBr and DOAc to *both* (*E*)- and (*Z*)-2-butene was found to be 84 ± 2% anti, the stereoselectivity remaining constant over a 100-fold concentration range of DBr. AdE3 mechanisms were considered to be the most consistent with all of the experimental data, the products being formed via the syn and anti transition states **1** and **2.**



1 2

Nu = Br or OAc

The identical stereoselectivities of addition of DBr and DOAc to the two 2-butenes was surprising. Limited stereochemical data indicated that the addition of DBr and DOAc to the 3-hexenes was essentially identical with that of the 2-butenes (84–85% anti); yet the additions to cyclopentene were found to be 96 ± 4% anti. Although there is some effect of alkene structure on stereoselectivity of addition, it was felt that initial complexing of the alkene with one molecule of hydrogen bromide resulted in polarization of the π system which dictated the stereoselectivity of the addition in the rate-determining transition state. Accordingly, we initiated a study of the stereoselectivity of various acid-catalyzed additions of acetic acid to (*E*)- and (*Z*)-2-butene, the results of which are reported herein.

Results

The deuterium chloride, deuterium bromide, methanesulfonic acid-*O-d*, and trifluoromethanesulfonic acid-*O-d* catalyzed additions of acetic acid-*O-d* to (*E*)- and (*Z*)-2-butene were studied. Owing to the essentially identical results obtained with the first three acids, the results of those studies will be discussed together, with the trifluoromethanesulfonic acid catalyzed reaction being discussed separately.

DCl, DBr, and CH_3SO_3D Catalyzed Additions. Solutions of the acid in acetic acid-*O-d* were prepared (see Experimental Sections) and the 2-butene added. The reactions were allowed to proceed to ~50% completion at 25 °C and the unreacted butene was pumped from the reaction mixture and analyzed by GLC. No diastereomerization or positional isomerization was detected. Mass spectral analysis of the butenes showed that no deuterium incorporation had occurred. The acetate fractions were isolated by extraction techniques and were purified by GLC or distillation. The acetates were converted to the corresponding alcohols by reduction with lithium aluminum hydride, and the diastereomeric composition of the alcohol fractions was determined by NMR techniques using a chemical shift reagent. The results of the stereochemical analyses are given in Table I.

The acetate fractions were also analyzed by mass spectrometry and compared with authentic 3-deuterio-2-butanol prepared by the deuterioboration of 2-butene followed by oxidation and acetylation. The relative intensities of the $M^{+\cdot}$, $(M+1)^{+\cdot}$, and $(M+2)^{+\cdot}$ peaks in the acetates formed in the acid-catalyzed addition reactions were within experimental error with authentic 3-deuterio-2-butyl acetate indicating the incorporation of only a single deuterium atom.

The diastereomeric stability of the 3-deuterio-2-butyl acetate in the presence of methanesulfonic acid in acetic acid was determined by monitoring the rotation of *l*-2-octyl acetate in acetic acid in the presence of methanesulfonic acid; no change in rotation was observed over a time period equivalent to that required for the addition reaction. (The optical stability of 2-octyl acetate and bromide in the presence of hydrogen bromide was previously established.)[1]

2-Butyl methanesulfonate was shown not to be formed during the addition reaction by monitoring reacting solutions by NMR. 2-Butyl methanesulfonate was prepared and subjected to acetolysis under the conditions of the addition reactions. The major products formed were the butenes (by

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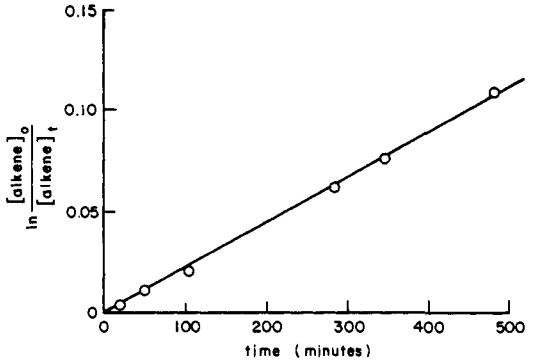


Figure 1. Triflic acid catalyzed addition of acetic acid to (*E*)-2-butene.

Table I. Stereoselectivities of Acid-Catalyzed Additions of Acetic Acid-*O*-*d* to (*E*)- and (*Z*)-2-Butene

Acid	catalyst (concn)	2-Butene	(concn)	% anti addn
DCl	(0.87 M)	(*E*)	(1.5 M)	84
DCl	(0.87 M)	(*Z*)	(1.5 M)	83
DBr	(0.55 M)	(*E*)	(~1.0 M)[a]	84[b]
CH_3SO_3D	(0.39 M)	(*E*)	(1.67 M)	84
	(0.63 M)	(*E*)	(1.67 M)	84
	(0.39 M)	(*Z*)	(1.67 M)	83
	(0.39 M)	(*Z*)	(1.67 M)	81

[a] Approximate concentration of a triply freeze-degassed solution of (*E*)-2-butene in acetic acid-*O*-*d*. [b] Previous result 84.0 ± 2.0% (see ref 1).

NMR). The rate of acetolysis is slower than the rate of acid-catalyzed addition of acetic acid and appeared to be autocatalytic, the initial rate of acetolysis being greater in the presence of methanesulfonic acid, but yet slower than acid-catalyzed addition.

Trifluoromethanesulfonic Acid Catalyzed Addition. Recovery of unreacted butene from addition reactions catalyzed by trifluoromethanesulfonic acid-*O*-*d* in acetic acid-*O*-*d* followed by GLC analysis indicated that both diastereomerization and positional isomerization had occurred, the extent of which increased with reaction time (see Table II). Separation of the recovered butene fractions by GLC followed by mass spectrometric analysis showed that H-D exchange had occurred (runs 2 and 4 in Table II). The stereoselectivity of the addition reaction decreased with increasing time of reaction (see Table II).

Pseudo-first-order rate constants were measured for the acid-catalyzed addition reactions (see Figure 1 and Table III). The H-D isotope effect for the catalyzed addition to (*Z*)-2-butene was found to be 1.8.[4] "Apparent rate constants"[5] for isomerization of (*Z*)-2-butene to the *E* isomer were also determined. The observed isotope effect of 2.0 is within experimental error with that for the addition.

Attempts to prepare 2-butyl trifluoromethanesulfonate at low temperature resulted in the apparent formation of the desired ester. However, warming to −20 to 0 °C resulted in the decomposition of the sulfonate and formation of a mixture of butenes. The butene mixture was isolated and analyzed by GLC showing the presence of 69% (*E*)- and 29% (*Z*)-2-butene and 2% 1-butene. In a control experiment, the optical rotation of a solution of *l*-2-octyl acetate in acetic acid in the presence of trifluoromethanesulfonic acid remained constant over a period of time longer than that required for the addition reaction to take place.

Table III. Rate Constants for Trifluoromethanesulfonic Acid Catalyzed Addition and Isomerization

Starting alkene	k_H, M^{-1} s^{-1} × 10^5	k_D, M^{-1} s^{-1} × 10^5
	Addition	
(*E*)	2.98	[a]
(*Z*)	2.75	1.53
	Isomerization[b]	
(*Z*)	3.87	1.93

[a] Not measured. [b] The "rate constant" for isomerization of (*E*)- to (*Z*)-2-butene could not be measured with reasonable accuracy owing to the small amount of isomerized alkene formed and the experimental uncertainty in the analysis.

Discussion

The lack of alkene diastereomerization, positional isomerization, and hydrogen-deuterium exchange in unreacted alkene in the addition reactions catalyzed by HCl, HBr, and CH_3SO_3H is fully consistent with the operation of concerted AdE3-type processes as proposed earlier,[1] and is inconsistent with the reversible formation of intermediate tight-ion pairs or free carbenium ions. Contrary to expectation, the stereoselectivity of the catalyzed addition reactions is not a function of relative acidity. These acids are relatively weak acids in acetic acid,[6] decreasing in the order $CH_3SO_3H > HBr > HCl$ spanning an acidity range of 10^2–10^3. The only effect of the relative acidities of the acids on the addition reactions is on the rate of reaction, the rates decreasing with decreasing acidity. The stereoselectivity of these addition reactions must therefore result from effects of alkene structure and/or solvent properties. Future efforts will be devoted to studies in these areas.

In contrast to the results derived with the weak acids described above, catalysis by the very strong acid trifluoromethanesulfonic acid[6,7] results in alkene diastereomerization, positional isomerization, and hydrogen-deuterium exchange, along with a much lower degree of stereoselectivity of addition. These results are consistent with the reversible formation of a tight-ion pair or free carbenium ion (see Scheme I). The slightly greater extent of anti addition can be attributed to steric shielding of the syn side of the carbenium ion in the tight ion pair. The changeover in mechanism must be due to the greater acidity of trifluoromethanesulfonic acid relative to the weaker acids discussed above.[8]

Table II. Trifluoromethanesulfonic Acid Catalyzed Addition of Acetic Acid-*O*-*d* to (*E*)- and (*Z*)-2-Butene

Run	2-Butene	% recovered butene: 1-Butene[a]	(*E*)-2-Butene	(*Z*)-2-Butene	% anti addn[b]
1	(*Z*)	0.5	12.4	87.1	60
2	(*Z*)	0.5	21.5 (25% d_1)	78.0	57
3	(*E*)	0.5	95.9	3.6	72
4	(*E*)	0.5	90.1	9.4 (20% d_1)	71

[a] Deuterium content not analyzed for. [b] Corrected for d_0 and d_2 content.

Table IV. Mass Spectral Relative Intensities of 3-Deuterio-2-butyl Acetates and 2-Butyl Acetate

Alkene precursor	Rel intensities at *m/e*				
	100	101	102	103	104
(*E*)		7.0	100.0	6.1	1.0
(*Z*)		7.2	100.0	6.0	1.0
Standard	1.0	100.0	6.1	1.0	

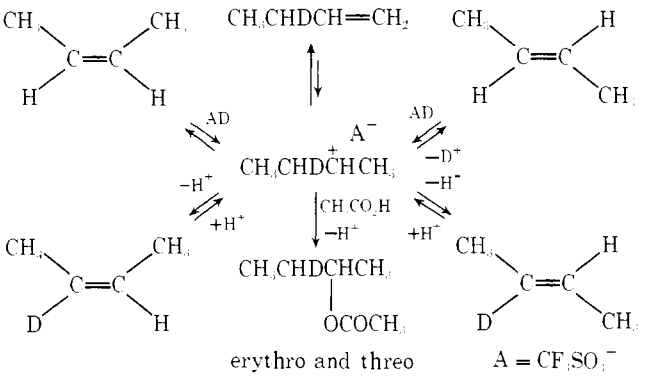
Table V. Mass Spectral Relative Intensities of 3-Deuterio-2-butyl Acetates Derived from Methanesulfonic Acid Catalyzed Additions

2-Butene	$[CH_3SO_3H]$, M	Rel intensities at *m/e*				
		100	101	102	103	104
(*Z*)	0.39		5.3	100.0	7.0	0.4
(*Z*)	0.39		2.8	100.0	7.3	0.8
(*E*)	0.39		4.9	100.0	6.8	
(*E*)	0.63		2.7	100.0	7.6	1.3
2-Butyl acetate		1.1	100.0	7.0	1.1	

Table VI. Optical Rotation of *l*-2-Octyl Acetate in Acetic Acid in the Presence of Methanesulfonic Acid

Time	Rotation, deg	Time	Rotation, deg
0	−0.537	93 h 44 min	−0.532
8 h 59 min	−0.534	311 h 56 min	−0.536
22 h 23 min	−0.542	800 h	−0.540

Scheme I



Experimental Section

Reagents. (*E*)-2-Butene (CP grade 99.0% min, found 99.0% (*E*), <0.1% 1-butene) and (*Z*)-2-butene (CP grade 99.8% min, found 98% (*Z*), <0.1% 1-butene) were purchased from the Matheson Co., Inc. Deuterium oxide (99.8% D) was obtained from Diaprep Inc. Methanesulfonic acid and trifluoromethanesulfonic anhydride were procured from Aldrich Chemical Co. Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-1,5-octanedionato)europium-d_{30}, Eu(fod)$_3$-d_{30}, was acquired from the Norell Chemical Co., Inc. Authentic samples of *erythro*- and *threo*-3-deuterio-2-butanols were prepared as described previously.[2]

Acetic Acid-*O*-*d*. A mixture of 302 mL (326.7 g, 3.2 mol) of freshly distilled acetic anhydride and 54.3 mL (60.19 g, 3 mol) of deuterium oxide was stirred in a round-bottomed flask equipped with a condenser and drying tube until the evolution of heat ceased. The acetic acid-*O*-*d* was then distilled (bp 116 °C) and stored in a stoppered flask in a drybox.

Acetic Acid. The procedure described for acetic acid-*O*-*d* was followed using distilled water instead of deuterium oxide.

Methanesulfonic Acid-*O*-*d*. Freshly prepared methanesulfonic anhydride[9] (3.48 g, 20 mmol) and 0.36 g (18 mmol) of deuterium oxide were mixed in a round-bottomed flask and stoppered. The flask

Table VIII. Optical Rotation of *l*-2-Octyl Acetate in Acetic Acid in the Presence of Trifluoromethanesulfonic Acid

Time	Rotation, deg
0	−0.670
47 h 46 min	−0.664
101 h	−0.672

Table IX. Kinetic Data for the Trifluoromethanesulfonic Acid Catalyzed Addition of Acetic Acid to (*Z*)-2-Butene[a]

Time, min	[2-Butyl acetate], M	Time, min	[2-Butyl acetate], M
0	0	244	0.093
11	0.006	586	0.205
66	0.024	1018	0.333
110	0.044	1249	0.374

[a] $[CF_3SO_3H]$ = 0.276 M, $[butene]_0$ = 0.8514 M.

Table X. Kinetic Data for the Trifluoromethanesulfonic Acid-*O*-*d* Catalyzed Addition of Acetic Acid-*O*-*d* to (*Z*)-2-Butene[a]

Time, min	[2-Butyl acetate], M	Time, min	[2-Butyl acetate], M
0	0	294	0.0681
3	0.0165	565	0.1102
29	0.0169	721	0.1352
122	0.0423		

[a] $[CF_3SO_3D]$ = 0.262 M; $[butene]_0$ = 0.7643 M.

Table VII. Mass Spectral Relative Intensities of 3-Deuterio-2-butyl Acetates from Trifluoromethanesulfonic Acid Catalyzed Addition

Run	Alkene	Rel intensities at *m/e*					
		100	101	102	103	104	105
1	(*Z*)		5.1	100	7.4	1.2	
2	(*Z*)	0.1	14.6	100	15.2	1.7	0.1
3	(*E*)		3.9	100	7.1	1.4	
4	(*E*)		11.6	100	6.7	1.2	
2-Butyl acetate		1.1	100.0	6.0	1.0		

Table XI. Kinetic Data for the Trifluoromethanesulfonic Acid Catalyzed Addition of Acetic Acid to (*E*)-2-Butene[a]

Time, min	[2-Butyl acetate], M	Time, min	[2-Butyl acetate], M
0	0	105	0.0183
20	0.0031	282	0.0543
50	0.0101	345	0.0664
80	0.0224	483	0.0933

[a] $[CF_3SO_3H] = 0.273$ M; $[butene]_0 = 0.9031$ M.

Table XII. Kinetic Data on the Triflic Acid Catalyzed Isomerization of (*Z*)-2-Butene in Acetic Acid at 25 °C[a]

Time, min	% *E*	% *Z*
0	2.00[b]	98.00
66	2.22	97.78
244	2.27	97.73
586	5.83	94.17
1018	9.41	92.59
1249	10.83	89.17
1479	12.09	87.91

[a] $[CF_3SO_3H] = 0.276$ M. [b] 2.00% *E* in *Z* starting material.

Table XIII. Kinetic Data on the Triflic Acid-*O-d* Catalyzed Isomerization of (*Z*)-2-Butene in Acetic Acid-*O-d* at 25 °C[a]

Time, min	% *E*	% *Z*
0	2.00[b]	98.00
3	2.34	97.66
29	2.59	97.41
122	2.82	97.18
294	2.88	97.12
565	4.06	95.94
721	4.55	95.45

[a] $[CF_3SO_3D] = 0.262$ M. [b] 2.00% *E* in *Z* starting material.

was heated at 85 °C for 1 week. The acid was then distilled (bp 128–129 °C, 1 mm) and stored in a stoppered flask in a drybox.

Methanesulfonic Acid. The procedure described for methanesulfonic acid-*O-d* was followed using distilled water instead of deuterium oxide.

Trifluoromethanesulfonic Acid-*O-d*. Trifluoromethanesulfonic anhydride (1.481 g, 5.25 mmol) and 0.102 g (5.12 mmol) of deuterium oxide were sealed in a 2-mL ampule and placed in a shielded sand bath at 85 °C for 2 weeks. The product was then distilled at reduced pressure and stored in a stoppered flask in a drybox.

Trifluoromethanesulfonic Acid. The procedure described for trifluoromethanesulfonic acid-*O-d* was followed using distilled water instead of deuterium oxide.

Deuterium Chloride Catalyzed Additions of Acetic Acid-*O-d* to 2-Butene. Acetyl chloride (7.51 g, 95.5 mmol) was added dropwise to a cooled solution of deuterium oxide (1.91 g, 95.4 mmol) in 95 mL of acetic acid-*O-d*. After the reaction was complete the solution was diluted to 100 mL with acetic acid-*O-d*. An aliquot of the deuterium chloride solution was removed, quenched with a known excess of sodium acetate, and back-titrated potentiometrically to determine the concentration of deuterium chloride (0.95 N). A 10-mL aliquot of the deuterium chloride solution was pipetted into an ampule and diluted to 11 mL with 2-butene to give a solution 0.87 N in DCl and 1.1 N 2-butene. The ampule was capped, cooled in a dry ice–acetone bath, and sealed under partial vacuum. The ampule was then placed in a 25 °C constant temperature bath.

After 100 days at 25 °C the reaction was quenched with a saturated aqueous solution of sodium acetate. Unreacted butene was recovered by trap-to-trap distillation on a vacuum line. The recovered butene fractions were analyzed by GLC on a tandem column of 8-ft 2.5% of 4:1 diethylene glycol adipate–bis-2-ethylhexyl sebacate on 60/80 Chromosorb G AW and 10-ft 20% silver nitrate–propylene glycol on 60/80 Firebrick at −10 °C.

The quenched reaction mixtures were extracted three times with 3-mL portions of pentane. The combined extracts were dried (K_2CO_3) and the pentane was removed by fractional distillation. The acetate fractions were purified by preparative GLC.

The mass spectrum of the purified acetate was compared with that of authentic 3-butyl acetate (see Table IV for relative intensity data).

Reduction of 3-Deuterio-2-butyl Acetate to 3-Deuterio-2-butanol. General Procedure. To a 5-mL suspension of lithium aluminum hydride (0.5 g, 13.0 mmol) in anhydrous ether in a 10-mL round-bottomed flask, equipped with condenser and magnetic stirring bar, was added dropwise a 2-mL solution of 3-deuterio-2-butyl acetate (100 mg, 0.85 mmol) in anhydrous ether. After 1 h the excess lithium aluminum hydride was destroyed by the dropwise addition of 3 mL of 1 N HCl (aqueous). The ether layer was removed and the aqueous layer was extracted twice with 2-mL portions of pentane. The pentane extracts were combined with the ether layer and dried over potassium carbonate. The alcohol was isolated from the solvent by preparative GLC on 10-ft 20% Carbowax 20M Firebrick 60/80 at 110 °C.

Determination of the Diastereomeric Composition of 3-Deuterio-2-butanols. 3-Deuterio-2-butanol (25 mg, 0.33 mmol) obtained from the lithium aluminum hydride reduction of the corresponding acetate was dissolved in 0.4 mL of deuteriochloroform in an NMR tube. Benzene (15 mg, 0.19 mmol) was then added to furnish a field/frequency lock. The solution was transferred to an NMR tube: 1.18 (d, 3), 0.93 (d, 3), 1.49 (m, 1), 3.76 (m, 1), 2.43 ppm (s). Eu(fod)$_3$-d_{30}, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium-d_{30}, was then added until the molar ratio of shift reagent to alcohol reached approximately 0.18. At this ratio the resonances of the methylene proton of the erythro isomer had separated from the resonances of the threo isomer. The threo isomer methylene proton had become partially overlapped with the 1-methyl protons. Noise decoupling of the 3-deuterium, $^1H\{^2H\}$ 15 359 Hz, followed by repeated integrations of the erythro methylene proton resonance region and of the 4-methyl proton resonance region gave data from which the amount of erythro isomer in the sample could be calculated. Corrections for 2-butanol-d_0 contaminations obtained from mass spectral analysis of the acetate were applied to obtain the actual diastereomer percentage (see Table I for results).

Deuterium Bromide Catalyzed Addition of Acetic Acid-*O-d* to (*E*)-2-Butene. The procedure employed previously[1] was used. The relative intensities of the $(M-1)^+$·, M^+·, $(M+1)^+$·, and $(M+2)^+$· of the acetate were 3.2:100.0:6.0:1.1. (See Table V for comparison with standard 2-butyl acetate. See Table I for the results of the stereochemical analysis.)

Methanesulfonic Acid-*O-d* Catalyzed Additions of Acetic Acid-*O-d* to the 2-Butenes. The 2-butene was condensed into a weighed amount of acetic acid-*O-d* in an ampule and the amount of alkene was determined by difference. A solution containing a known amount of methanesulfonic acid-*O-d* was added and the resulting solution was quickly diluted to 10 mL. The ampule was then sealed under vacuum and placed in a constant temperature bath at 25 °C. After 36 days the

Table XIV. Attempted Syntheses of 2-Butyl Trifluoromethanesulfonate

Run	Solvent	Temp, °C	$(CF_3SO_2)_2O$, mmol	2-Butanol, mmol	Pyridine, mmol
1	Pyridine	−80	1.9	1.9	
2	Ether	−80	1.7	1.7	1.7
3	$CDCl_3$	25	0.5	0.5	0.5
4	Ether	−80	1.5	1.5	1.5 mmol of 2,6-lutidine

reaction solution was quenched with saturated aqueous sodium acetate. The unreacted alkene was isolated by trap-to-trap distillation and analyzed by GLC as described above. No isomerization was indicated.

The acetate fractions were isolated as described above and analyzed by mass spectrometry (see Table V).

Control Experiment on the Racemization of *l*-2-Octyl Acetate by Methanesulfonic Acid in Acetic Acid. *l*-2-Octyl acetate (0.8786 g, 5.1 mmol) and methanesulfonic acid (0.2028 g, 2.11 mmol) were dissolved in 10 mL of acetic acid. The optical rotation was recorded periodically. The observed rotations are listed in Table VI.

Acetolysis of 2-Butyl Methanesulfonate in the Absence and Presence of Methanesulfonic Acid. 2-Butyl methanesulfonate[10] (78.9 mg, 0.563 mmol) was dissolved in 0.3 mL of acetic acid in an NMR tube. Methanesulfonic acid-*O-d* (5.3 mg, 0.055 mmol) was added by syringe and the solution was diluted to 0.5 mL. The tube was cooled in dry ice–acetone and then sealed under vacuum and placed in a 25 °C bath. Qualitative NMR spectra were recorded periodically over a span of 60 days. The 2-butyl methanesulfonate was slowly transformed to 2-butyl acetate and butene as indicated by the appearance of peaks at δ 4.80 and 5.40, respectively. The alkenes were the predominant products.

Trifluoromethanesulfonic Acid-*O-d* Catalyzed Addition of Acetic Acid-*O-d* to 2-Butene. The procedure described previously for the methanesulfonic acid-*O-d* catalyzed additions was followed. The recovered alkene was analyzed by gas chromatography; the results are tabulated in Table II. The alcohol, obtained from the acetate as described above, was analyzed by NMR; the results are listed in Table II.

Mass spectral data for the acetate fractions are given in Table VII.

Control Experiment on the Racemization of *l*-2-Octyl Acetate by Trifluoromethanesulfonic Acid in Acetic Acid. *l*-2-Octyl acetate (0.460 g, 2.67 mmol) and trifluoromethanesulfonic acid (0.363 g, 1.29 mmol) were dissolved in 5 mL of acetic acid. The optical rotation of the solution was recorded periodically. No change in optical rotation occurred over 4 days (see Table VIII).

Kinetic Studies of Triflic Acid Catalyzed Addition of Acetic Acid to (*Z*)-2-Butene. (*Z*)-2-Butene (2.389 g, 42.20 mmol) was condensed into 20 mL of acetic acid in a 50-mL volumetric flask. *n*-Nonane (0.3753 g, 2.93 mmol) was added as an internal standard. A solution of 2.070 g (13.79 mmol) of triflic acid in 25 mL of acetic acid was added and the volume was adjusted to 50 mL. The flask was capped with a serum cap and was placed in a 25 °C constant temperature bath. Aliquots (0.5 mL) were periodically removed by syringe and quenched in *N,N*-dimethylaniline. A 40-μL sample of each quenched aliquot was analyzed by GLC on 12-ft 20% Carbowax 20M on Firebrick 60/80 at 110 °C. The formation of acetate was followed by comparison of the peak areas of the product acetate and *n*-nonane. The data obtained are shown in Table IX.

The rate constant for addition was calculated for an assumed pseudo-first-order rate law:

$$R = k'[\text{butene}] = k[CF_3SO_3H][\text{butene}]$$

assuming that $[\text{butene}]_t = [\text{butene}]_0 - [\text{2-butyl acetate}]_t$.

Kinetic data for the catalyzed addition in acetic acid-*O-d* are given in Table X.

Kinetic data for the trifluoromethanesulfonic acid catalyzed addition of acetic acid to (*E*)-2-butene are given in Table XI.

Kinetics of Triflic Acid Catalyzed Isomerization of (*Z*)-2-Butene in Acetic Acid at 25 °C. During the kinetic runs for addition of acetic acid to (*Z*)-2-butene, analysis of the unreacted butenes was carried out using the tandem column described previously. Tables XII and XIII list the data for isomerization of (*Z*)-2-butene in acetic acid and acetic acid-*O-d*.

Attempted Synthesis of 2-Butyl Trifluoromethanesulfonate. Under the conditions listed in Table XIV, attempts were made to synthesize 2-butyl trifluoromethanesulfonate. The procedures involved the addition of dry ice–acetone cooled solution containing 2-butanol and pyridine to the dry ice–acetone cooled solution of trifluoromethanesulfonic anhydride. Following filtration to remove the pyridinium salt, isolation of the 2-butyl trifluoromethanesulfonate was attempted by reduced pressure distillation (run 1) or by reduced pressure solvent evaporation. Run 2 gave an uncharacterized colorless oil which at 0 °C promptly decomposed with evolution of butene.

Determination of Butene Isomer Distribution from 2-Butyl Trifluoromethanesulfonate in the Presence of Acetic Acid. Trifluoromethanesulfonic anhydride (0.981 g, 3.48 mmol) was dissolved in 2 mL of anhydrous ether and cooled to −78 °C. 2-Butanol (0.258 g, 3.48 mmol) was dissolved in 1 mL of anhydrous ether and added dropwise slowly to the cooled solution of anhydride. Immediately, 7 mL of anhydrous acetic acid was added and the reaction mixture was allowed to warm to room temperature. Gas bubbles began to appear upon warming. Using reduced pressure the evolved gases were drawn off into a trap cooled in liquid nitrogen. Gas chromatographic analysis of the gases gave the following isomer distribution: (*E*)-2-butene, 69%; (*Z*)-2-butene, 29%; 1-butene, 2%.

References and Notes

(1) Submitted to the University of Notre Dame for the partial fulfillment of the requirements for the Ph.D. by J.F.G.

(2) D. J. Pasto, G. R. Meyer, and B. Lepeska, *J. Am. Chem. Soc.*, **96**, 1858 (1974).

(3) It has been claimed that the rates of sulfuric, perchloric, and methanesulfonic acid catalyzed acetic acid addition to cyclohexene in acetic acid correlate with the acidity function: R. Corriu and J. Guenzet, *Tetrahedron*, **26**, 671 (1970).

(4) The magnitude of this isotope effect is similar to that reported for acid-catalyzed additions of acetic acid-*O-d* to cyclohexene (1.42–1.52) reported in the reference in footnote 3.

(5) The rate constants given are for the appearance of the isomerized alkene and are not the rate constants for protonation of the alkene.

(6) I. M. Kolthoff and A. William, *J. Am. Chem. Soc.*, **56**, 1007 (1934); T. Gramstad, *Tidsskr. Kjemi, Bergves. Metall.*, **19**, 62 (1959); *Chem. Abstr.*, **55**, 12739*e* (1960). C. H. Rochester, "Acidity Functions", Academic Press, New York, N.Y., 1970, p 207, and references cited therein.

(7) R. M. G. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1183 (1976).

(8) During the completion of our studies the results of a study of the trifluoromethanesulfonic acid catalyzed addition of acetic acid-*O-d* to cyclopentene was reported (see ref 7). It was reported that a "higher boiling product" was formed which was specified as being cyclopentyl triflate. It was also reported that the catalyzed addition of acetic acid to cyclohexene and cyclopentene was reversible and occurred in a 50:50 syn–anti ratio, yet no H–D incorporation was observed. A detailed analysis of the H–D isotope effects for protonation and deprotonation and consideration of the extent of isomerization observed in our studies resulted in a calculated deuterium incorporation of only $\gtrsim$2%. Private communication with the author revealed that ~2% deuterium incorporation in the cyclopentene would not have been detectable by the low-resolution techniques employed. We repeated the experiment as reported in ref 7 and carried out a high-resolution mass spectral analysis on the parent ion of cyclopentene and found ~1.6% deuterium incorporation. Attempts to prepare and detect cyclopentyl triflate by reaction of cyclopentanol with trifluoromethanesulfonic anhydride resulted in formation of only cyclopentene at temperatures $\gtrsim$0 °C. We therefore conclude that the trifluoromethanesulfonic acid catalyzed addition of acetic acid to cyclopentene occurs in a manner identical with that proposed in this paper.

(9) V. C. Barry and P. W. D. Mitchell, *J. Chem. Soc.*, 3723 (1953).

(10) G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.*, **22**, 479 (1957).