J. Org. Chem. **1994**, *59*, 163–168

Secondary and Tertiary 2-Methylbutyl Cations. 2. Addition of Trifluoroacetic Acid to Methylbutene[1]

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Received August 17, 1993[•]

The reaction of 3-methyl-1-butene (**4**), 2-methyl-1-butene (**5**), and 2-methyl-2-butene (**6**) in trifluoroacetic acid (TFA), neat or buffered with potassium trifluoroacetate, and in 74:26 TFA–MeCN was studied. Alkenes **5** and **6**, which form a tertiary carbocation (**2**) upon hydronation, react 6.6×10^4 and 5.8×10^4 times faster than **4** (TFA–MeCN, 25 °C). The rates in TFA-*d* gave KIEs of 6.8 (**4**, 26.5 °C), ca. 5 (**5**, −18 °C), and 3.9 (**6**, −18 °C). The esters 3-methyl-2-butyl trifluoroacetate (**7**) and 2-methyl-2-butyl trifluoroacetate (**8**) are formed from **4** in the same ratio in TFA and in TFA-*d* (ca. 53:47), thus proving that **4** reacts entirely by a carbocationic mechanism, with no measurable contribution from a molecular addition. In the presence of *p*-toluenesulfonic acid the reaction of **4** at 0 °C forms significant amounts of 3-methyl-2-butyl tosylate (**3**), and the final ratio of **7**:**8** was close to that observed in the solvolysis of **3**. The different product distributions in solvolyses and alkene hydronations observed before are brought about most probably by the different anions present in the tight ion pairs rather than by differences in the nature of the intermediate carbocations. The reaction in TFA-*d* showed that the 3-methyl-2-butyl cation (**1**) undergoes methyl shift to an extent (32%) smaller than in the solvolysis of the tosylate **3** before being trapped by the solvent. Extensive H/D exchange between the solvent and ester **8** prevented us from ascertaining whether skeletal rearrangement had occurred in the latter as well. Formation of the 2-methyl-2-butyl cation (**2**) from **5** and **6** is reversible, leading to partial isomerization of **5** to **6** in the initial stages of the reaction. Therefore the quoted rate ratios of **5** to **6** to **4** are minimum values. Hydron loss from the ethyl group of **2** is 9.3 ± 1.8 faster than hydron loss from a methyl group. In 74:26 TFA–MeCN, cation **2** is trapped by the two solvents in a 12.6:1 ratio at 25 °C.

Introduction

Trifluoroacetic acid (TFA) was demonstrated to be a very good medium for the generation of carbocations from alkenes in homogeneous solution.[3] The reaction mechanism of the addition was classified as $A\text{-}S_E2$, with hydron transfer as the rate-determining step.[4] Initial formation of a π-complex was also proposed by some authors,[3b,e,h] but was refuted by others.[3i] A molecular ("cyclic") addition mechanism was claimed for TFA addition to limonene in cyclohexane,[5] but intervention of carbocations was demonstrated for the reaction of 7,7-dimethylnorbornene.[3f] Moreover, reaction of alkynes was reported to lead to vinyl cations,[6] and a distinct hydron transfer step was shown to occur in the cleavage of three-membered rings by TFA in chloroform when stabilized carbocations result.[7]

In the preceding paper of this series[1a] we reported on the generation of the 3-methyl-2-butyl cation (**1**) and its tertiary isomer 2-methyl-2-butyl cation (**2**) by the solvolysis of 3-methyl-2-butyl tosylate (**3**). To understnad better the formation and reactivity of these ions we undertook a parallel investigation of the addition of trifluoroacetic acid to the isomeric methylbutenes, 3-methyl-1-butene (**4**), the precursor of **1**, and 2-methyl-1-butene (**5**) and 2-methyl-2-butene (**6**), precursors of **2**. At the same time, noticing that no alkenes appear among the products of solvolysis of **3** in TFA,[1a] whereas in the acetolysis of **3** olefins **4**–**6** represent the major products,[8] we decided that determining the reactivity of these alkenes in TFA represents an interesting objective.

We report here on the rates and products of these addition reactions. As it had been reported that small amounts of water in TFA increase slightly the rate of addition to other alkenes, even though the effect was small,[3b] we used TFA containing a small amount (around 1%) of its anhydride.

Results and Discussion

The reaction rate of 3-methyl-1-butene (**4**) with TFA, pure or buffered with 0.15 M of its potassium salt, could be conveniently measured at two temperatures. By contrast, isomers **5** and **6** were consumed entirely in less than a minute at −18 °C. Nonetheless, approximate values of the solvolysis rate constants of the latter were obtained

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[•] Abstract published in *Advance ACS Abstracts*, December 1, 1993.

(1) (a) For part 1, see: *J. Org. Chem.*, preceding paper in this issue. (b) Reported in part at the International Symposium on Carbocations and other Reactive Intermediates, Tübingen, Germany, Aug 18, 1988.

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Table 1. Rates of TFA Addition to Alkenes[a]

alkene	reagent	temp, °C	k_1[b] s^{-1}	k_{rel}		
4	TFA (buffer)[c]	−0.7	5.2×10^{-6}			
		26.5	8.5×10^{-5}			
		−18.0	6.5×10^{-7} [d]	1		
		25.0	7.4×10^{-5} [d]			
	TFA	26.4	5.3×10^{-5}			
	TFA–TsOH[e]	0.0	(4×10^{-4})[f]			
	TFA-*d*	26.4	7.8×10^{-6}			
	74/26 TFA–MeCN[g,h]	30.1	2.41×10^{-6}			
		44.9	1.05×10^{-5}			
		−18.0	6.3×10^{-9} [d]		1	
		25.0	1.4×10^{-6} [d]			1
5[i]	TFA (buffer)	−18.6	0.21	3.2×10^5		
	TFA	−18.0	0.19			
	TFA-*d* (buffer)	−17.5	0.043			
	74/26 TFA–MeCN[g,j]	−25.9	1.77×10^{-3}			
		−18.3	2.72×10^{-3}			
		−9.8	7.5×10^{-3}			
		−18.0	3.4×10^{-3} [d]		5.4×10^5	
		25.0	9.3×10^{-2} [d]			6.6×10^4
6[i]	TFA (buffer)	−17.7	0.15	2.3×10^5		
	TFA	−17.9	0.098			
	TFA-*d*	−18.1	0.025			
	74/26 TFA–MeCN[g,k]	−25.9	5.1×10^{-4}			
		−18.0	1.36×10^{-3}		2.2×10^5	
		−9.8	3.1×10^{-3}			
		25.0	8.1×10^{-2} [d]			5.8×10^4

[a] Determined by GLC. [b] Pseudounimolecular (solvolytic) rate constant. [c] $\Delta H^{\ddagger}$ = 16.1 kcal/mol, $\Delta S^{\ddagger}$ = −23.5 cal/mol·deg, calculated with the program from ref 9. [d] Calculated from the data at other temperatures. [e] Molar ratio TsOH:4 = 1:1. [f] Estimated value, see Experimental Section. [g] By volume. [h] $\Delta H^{\ddagger}$ = 18.4 kcal/mol, $\Delta S^{\ddagger}$ = −23.5 cal/mol·deg. [i] Apparent rate constants, disregarding the return to 5 and 6 from 1. [j] $\Delta H^{\ddagger}$ = 11.1 kcal/mol, $\Delta S^{\ddagger}$ = −25.9 cal/mol·deg. [k] $\Delta H^{\ddagger}$ = 14.0 kcal/mol, $\Delta S^{\ddagger}$ = −16.6 cal/mol·deg.

by analysis of mixtures quenched after 5–15 s at this temperature. We could not go lower than that because TFA started to freeze. The results of all rate measurements are shown in Table 1.

$Me_2CHCH{=}CH$	$Me(Et)C{=}CH_2$	$Me_2C{=}CHMe$
4	5	6

We were able to compare the reactivities of alkenes 4, 5, and 6 by extrapolating[9] the rates for 4 to −18 °C. For a better comparison, we conducted the addition in a mixture 74:26 by volume of TFA and acetonitrile as well. The predominance of TFA in the mixture assures the maintenance of the anion-stabilizing properties of the solvent, judged to be essential for manifestation of carbocationic reactivity.[10] Under these conditions, the reaction is slowed down 50 times or more but the ratios of rate constants are about the same as in neat TFA. Alkenes 5 and 6, which give upon hydronation the tertiary cation 2, react faster than 4 by a factor of 6×10^4 at room temperature. The slightly higher reactivity of 5 over 6 can be traced to the difference in stability between the starting alkenes.

The addition was also run in TFA without addition of potassium trifluoroacetate. The rates were slower here, but the differences were close to, and in one case smaller than, the combined uncertainties in the rate constants. Nonetheless, the fact that the variations were in the same direction for all three reactants deserves notice, especially because an earlier report indicated that the rate of TFA addition to 1-hexene was essentially the same in the presence or absence of sodium trifluoroacetate.[3b] Likewise, the addition of acetic acid to norbornadiene was not affected by sodium acetate.[11] The presence of an equivalent amount of *p*-toluenesulfonic acid (TsOH) in TFA increases significantly the rate of reaction, in agreement with findings for other alkenes.[3b,12]

The existence of a methyl group and a tertiary hydrogen which both can migrate (and, as shown below, do so) adjacent to the double bond has no special effect upon the rate of addition. The reaction of 4 is about twice as fast as addition to propene (reported half-life ca. 300 min[12]) and 1.5 times faster than addition to 1-hexene.[3a] This is in line with the observation that double-bond protonation involves less anchimeric assistance than tosylate solvolysis[13] and with the reports that even for 3-methyl-2-butyl tosylate (3) no substantial rate acceleration attributable to neighboring group participation was observed.[1a,8a,14] On the other hand, the study of TFA addition to 4,4-dimethyl-1-pentene showed that the reaction does not have significant steric demands.[3c]

Reaction in deuterated TFA revealed large kinetic isotope effects (KIEs): 6.8 for 4 at 26.4 °C, about 5 for 5 at −18 °C, and 3.9 for 6 at the same temperature (Table 1). KIEs around 2 (or for that matter greater than 1)[15] had been considered to demonstrate that the reaction involves a rate-determining hydron transfer from the acid to the double bond with the formation of a carbocation.[3i,5,16]

The reaction products from 4 were the secondary 2-methyl-3-butyl trifluoroacetate (7) and the hydrogen-

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shifted 2-methyl-2-butyl trifluoroacetate (8, eq 1). The tertiary ester 8 was the sole product from 5 and 6 (eq 2).

$$4 \rightarrow \underset{7}{Me_2CHCHMeOCOCF_3} + \underset{8}{Me_2C(OCOCF_3)CH_2Me} \quad (1)$$

$$5, 6 \rightarrow 8 \quad (2)$$

To determine the composition of the reaction products from 4, aliquots of the reacting solution were withdrawn at regular intervals, quenched in a mixture of 2 N sodium hydroxide and hexane, and analyzed by capillary column GLC. The ratio of 7 to 8 after 15% conversion was about 43:57, and it increased to 53:47 (±2) after about 4 half-lvies. No further change was seen after 10 and after 50 half-lives; therefore the variation with reaction time could not be due to conversion of 8 to 7. Moreover, no interconversion of isomers was seen when pure 7 or 8 was held in TFA under the same conditions. Also, the ratio after 10 half-lives was the same when quenching was effected with potassium carbonate in water and ice, showing that NaOH did not induce elimination or ester hydrolysis. Most probably, there is a difference in the solubility of the two esters in water, which has a more important effect at the low total concentrations present after small conversions. The same product ratio was obtained from the reaction at −0.7 °C (after 3 half-lives) and at 51.8 °C.[17]

The large amount of 7 observed here is in contrast with the finding of a 98.5:1.5 ratio of 8 to 7 from 3-methyl-2-butyl tosylate (3).[1a] There was the possibility that ester 7 was formed largely by a molecular addition of TFA[5,11,18] or a concerted attack of two molecules of TFA on 4 without the invervention of a carbocation.[19] Such a mechanism cannot be reconciled with the large solvent KIE observed (the molecular additions have KIEs close to 1[4,5,15,16]), but one could still argue that part of the alkene reacts by hydron transfer with an even larger isotope effect than 6.8 and gives mostly 8,[1a] whereas another part reacts by a molecular mechanism with KIE close to 1[5] and gives 7. If this were the case, reaction in TFA-*d* should exhibit a drastically different product distribution, but we obtained from the reaction in TFA-*d* the same 7:8 ratio (54:46) as from the reaction run in unlabeled TFA. In addition, the sizable molecular rearrangement found in 7 formed in TFA-*d* (see below) proves that 7 is formed from a carbocation.

A different composition of the product had also been reported for TFA addition to 1-hexene and trifluoroacetolysis of 2-hexyl tosylate, the latter reaction forming more of the rearranged 3-hexyl trifluoroacetate.[3b] It was then concluded that the two reactions do not proceed entirely through the same intermediate ion.[3b] The same conclusion was reached for the reactions 1-butene and 2-butanol in 0.55 M perchloric acid, which also gave different product distributions.[20,21] To test this mechanistic model, we examined the reaction of 4 in TFA containing *p*-toluenesulfonic acid in a molar ratio TsOH/4 of 1:1 at 0 °C, by ^{1}H NMR spectroscopy. Under these conditions the addition to 4 had a half-life of about 30 min, thus being more than three times faster than the solvolysis of 3 (half-life 100 min at 0 °C) and 68 times faster than the uncatalyzed addition. A more significant feature of the reaction was that 3 was formed in the early stages of the reaction in an amount about equal to the trifluoroacetate esters. This result indicated that ion 1 was trapped by the tosylate anion in the tight ion pair resulting from the hydron transfer from the acid to 4. Throughout the reaction the addition product was mostly the tertiary ester 8 with very little of 7. Integration of the NMR spectrum of the final reaction mixture showed a content of 7 in the ester mixture of about 7–9%. This value was larger than the ratio determined by GLC in the solvolysis product from 3 (1.5%) but it was not far from the ratio measured for the same reaction product by ^{19}F NMR spectroscopy (4%) and it was much different from the quantity formed in the uncatalyzed addition.

We interpret these results to mean that the differences in ratios of products from solvolyses and alkene hydronation observed by us and by others before us are not brought about by differences in the intermediate carbocations but by differences in the nature of the anion present in the tight ion pair. The properties of the anion determine the extent of movement of the carbocation in the ion pair, as well as the lifetime of the ion pair in a given solvent.

That the carbocation 1 formed by hydronation of 4 is the same as the one formed in the solvolysis of 3 was also indicated by the presence of skeletal rearrangement in the secondary ester 7 (eq 3).

$$4 + \text{TFA-}d \rightarrow \underset{7\text{-}1\text{-}d}{Me_2CHCH(OTFA)CH_2D} + \underset{7\text{-}4\text{-}d}{DCH_2CHMeCH(OTFA)Me} + 8\text{-}d \quad (3)$$

The extent of rearrangement was difficult to determine accurately because the extensive exchange occuring in the tertiary ester 8 during the long reaction times necessary for the reaction of 4 resulted in the isotope dilution of the acid. The intensity ratio in the mass spectrum of the ions with *m/z* 113 (9) and *m/z* 114 (9-*d*)[1a,22] was 35:65, but *m/z* 113 results both from the molecules of 7 formed from 2 after migration of a methyl (eq 4) and from the molecules of 7 formed by addition of unlabeled TFA to 4 (eq 5). The isotope content of 7 after exchange could not be determined by the procedure used in our other study[1a] because no molecular ion peak was observed for 7 in the EI spectrum.[22a] To circumvent this limitation, we used chemical ionization MS[23] with isobutane as reactive gas. This procedure leads to generation of a reasonably intense peak for the (M − Me) ion (10), which was very weak in the EI spectrum. For the TFA-*d* addition product this ion appears at *m/z* 169 (10) and *m/z* 170 (10-*d*) in a 69:31 ratio, but now it is the deuterium-containing ion which results from the methyl-

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[17] A change in composition of reaction products during the reaction was previously observed in the addition of TFA to 1-hexenes (ref 3b), but in that case it was the proportion of rearranged ester, 3-hexyl trifluoroacetate, which increased, because isomerization of 1-hexene to 2-hexene occurred at a rate comparable with formation of 2-hexyl trifluoroacetate from 1-hexene.

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migrated ester (*7-4-d*, eq 4), whereas the unlabeled ion results from unrearranged *7-1-d* (eq 6) and from **7** obtained by addition of unlabeled TFA to **4** (eq 5):

$$\underset{\mathbf{9}\ (m/z\ 113)}{CF_3COOCH^+Me} \leftarrow \mathbf{7}\text{-}4\text{-}d \rightarrow \underset{\mathbf{10}\text{-}d\ (m/z\ 170)}{DCH_2CHMeCH^+OCOCF_3} \qquad (4)$$

$$\mathbf{9}\ (m/z\ 113) \leftarrow \mathbf{7} \rightarrow \mathbf{10}\ (m/z\ 169) \qquad (5)$$

$$\underset{\mathbf{9}\text{-}d\ (m/z\ 114)}{CF_3COOCH^+CH_2D} \leftarrow \mathbf{7}\text{-}1\text{-}d \rightarrow \underset{\mathbf{10}\ (m/z\ 169)}{MeCHMeCH^+OCOCF_3} \qquad (6)$$

The extent of rearrangement (percentage of *7-4-d* in its mixture with *7-1-d* in the product) was calculated from these data as approximately 32%. The degree of skeletal rearrangement in the tertiary ester **8** formed in the reaction of **4**, if any, cannot be deduced from our experiments.[24]

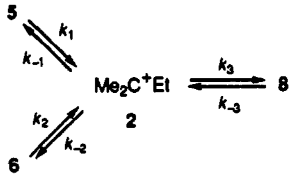
All these results indicate that **4** is hydronated in TFA to the ion pair of **1** with trifluoroacetate. The lower extent of hydrogen and methyl migration relative to those found in the solvolysis of the 3-methyl-2-butyl tosylate (**3**)[1a] indicates that the trifluoroacetate ion pair is "tighter" or shorter-lived than the tosylate ion pair. We can note that in the buffered solution the trifluoroacetate anion is the nucleophile in both cases, but it is an external nucleophile in solvolysis and the counterion of the ion pair in the addition reaction. Also, considering that hydrogen and methyl migration occur from different conformations of cation **1**, it is possible that this ion is formed with different rotamer distributions from alkene hydronation and from tosylate solvolysis.[25]

The isotope exchange occuring in the tertiary ester **8** indicates that this ester solvolyzes easily, which could be expected on the basis of the established reactivity of tertiary alkyl esters of perfluorocarboxylic acids.[26]

In the pioneering studies of TFA addition to alkenes, Peterson has found that the reaction leads to an equilibrium between alkene and ester. For 2-methyl-2-butene (**6**), the equilibrium was reached at 1.1 to 1.2% alkene in the mixture.[3d] Later, it was reported that methylenebicyclo[2.2.2]octane and 2-methyl-2-bicyclo[2.2.2]octene are interconverted in TFA before they form the tertiary trifluoroacetate.[3g] On the other hand, other workers had concluded that alkenes **5** and **6** do not interconvert during acid-catalyzed hydration, because no **5** was observed when the reaction of **6** was interrupted after 50% conversion.[27] Our observation of isotope exchange in the methyl and ethyl groups of **7** in TFA-*d* indicates that addition to both **5** and **6** is reversible and the two isomers do, therefore, interconvert.

The isotope exchange in **8** results from elimination from cation **2** followed by addition of TFA-*d* to **5** and **6** thus formed. The incorporation of D in a methyl group and in the ethyl group can be treated as first-order processes, and the ratio of the two rate constants equals the ratio of hydron loss from the respective groups in **2**. We determined the isotope distribution in **8** from the isotope content of ion *m/z* 169 (M − Me) and *m/z* 155 (M − Et). In two low conversion experiments described in the Experimental Section, the ratios of rate constants of deuteration of the ethyl group and of a methyl group were evaluated at 11.1 and 7.4, respectively. The average value, 9.3 ± 1.8, approximates the ratio of rate constants for elimination from the ethyl group and from a methyl group of **2**.

In the experiments of TFA addition to **5**, small amounts of **6** were observed by GLC in the reaction mixture quenched before the completion of the reaction. The variation of the ratio between the two alkenes with conversion in the reaction of **5** was seen better in 74:26 TFA–MeCN (see Experimental Section). No **5** could be positively identified, however, in the reacting mixtures from **6** and TFA or TFA–MeCN. The fact that cation formation from TFA addition to **5** and **6** is not strongly reversible is consistent with the large KIE observed.[25] The reaction of alkenes **5** and **6** can be described by eq 7, in



(7)

which the TFA and the trifluoroacetate anion were omitted for simplification.

The process of eq 7 was analyzed for our best kinetic data, obtained from the reactions of **5** and **6** in TFA–MeCN at −25.9 °C. Under these conditions ionization of **8** (k_{-3}) can be disregarded and the unknowns are k_1, k_2, $k_{-1}/(k_{-1} + k_{-2} + k_3)$, and $k_{-2}/(k_{-1} + k_{-2} + k_3)$. Application of the steady state approximation allows the analysis of data by three simultaneous rate equations (concentration changes of **5**, **6**, and **8**, the latter being the negative of the sum of the other two). An iterative fitting of the experimentally determined concentrations of the three compounds gave values for k_1 and k_2 which are larger than the values of Table 1 by less than the experimental errors. The fraction of return from **2** formed from either precursor to **6** was 0.12, whereas the fraction of return to **5** was found 0.03, but such a small value is unreliable. It can be noted, however, that from the isotope exchange experiments discussed above it follows that 2–3% of **2** returns to **5**; then, 12% returns to **6** and the remainder (85–86%) forms **8**.

Finally, we found that ion **2** becomes separated enough from the anion to be trapped by another solvent, in our case MeCN. Thus, *N*-(2-methyl-2-butyl)acetamide (**11**) was identified by GLC and GC-MS, by comparison with an authentic sample, in the quenched product from the reaction of **6** in 74:26 TFA–MeCN at 25 °C. The ratio of GLC peak areas for **8** and **11** was 12.6:1.

Conclusions

Addition of TFA to 3-methyl-1-butene (**4**) is entirely carbocationic and forms the secondary 3-methyl-2-butyl cation (**1**), which undergoes competitive hydrogen shift to the tertiary 2-methyl-2-butyl cation (**2**) and methyl shift (automerization) before being captured by the solvent as 2-methyl-2-butyl trifluoroacetate (**8**) and 3-methyl-2-butyl trifluoroacetate (**7**), respectively. The first intermediate of the reaction is a tight ion pair; reaction of **4** with TsOH in TFA leads to a significant ion pair return to the 3-methyl-

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[24] This information could be obtained from a study of 3-methyl-1-butene labeled with C-13 reacting in unlabeled TFA. Such an investigation is beyond our current means.

[25] Observation made by a reviewer of the manuscript.

[26] Fărcaşiu, D.; Jähme, J.; Rüchardt, C. *J. Am. Chem. Soc.* **1985**, *107*, 5117.

[27] Levy, J. B.; Taft, R. W., Jr.; Hammett, L. P. *J. Am. Chem. Soc.* **1953**, *75*, 1253.

2-butyl tosylate (**3**). The extent of methyl migration found in **7** (32%) is less than in the solvolysis of **3** (42%)[1a] and indicates that the symmetrical 1-protonated-2,3-dimethylcyclopropane does not represent the structure of **1** formed in solution from either precursor. It is possible, however, that the structure of this ion be different in the gas phase. The role of solvation and especially ion pairing might be important here.

The different product distribution (**7**:**8**) and extent of methyl migration found in **7** resulting from TFA addition to **4** and from trifluoroacetolysis of tosylate **3** are brought about most probably by the different anions present in the ion pair rather than by differences in the nature of the intermediate carbocations. We believe that our observations are relevant for other carbocations and carbocationic reactions as well.

Addition of TFA to the other two methylbutenes (**5** and **6**) is about 5 orders of magnitude faster than addition to **4** and forms cation **2** in a reversible reaction. A weakly nucleophilic aprotic solvent, MeCN, competes with TFA for the capture of this carbocation.

Experimental Section

General Procedure. Reagent grade chemicals were used as purchased unless stated otherwise. The analytical procedures were described elsewhere.[1a]

Water Removal from TFA-*d*. Commercial TFA-*d* (99.5% D, 50 mL) was treated with trifluoroacetic anhydride (3.5 mL) overnight. Nothing distilled from the mixture upon heating to 60 °C. After a second treatment with 5 mL of anhydride, almost 5 mL of distillate (mostly unreacted anhydride) was collected between 50 and 60 °C. The protium content of the dried acid remaining in the flask was established as 1.3% by ^1H NMR in dry (distilled from CaH_2) THF with 1,3,5-tribromobenzene as integration standard. Alternatively, anhydrous TFA-*d* was prepared by reaction of D_2O with an excess of TFA anhydride.

Additions to 3-Methyl-1-butene (4). In a typical run, **4** (0.2343 g, 3.35 mmol) was mixed with 2,3-dimethylpentane (DMP, 0.2469 g, 2.47 mmol) as GLC integration standard. Buffered TFA (10 mL) was placed inside a drybox in a 25-mL round-bottomed flask which was then fitted with a 4-mm-bore stopcock. A rubber septum was placed over the outer joint of the stopcock; then the flask was taken out of the drybox and placed in the thermostated bath. The hydrocarbon mixture equilibrated at the same temperature as the acid was injected into the flask with a syringe with long needle, through the septum and the open stopcock. The flask was swirled and a 0.5-mL sample was taken immediately with another syringe, after which the stopcock was closed. The acid sample was injected into a separatory funnel containing ice, 2 N aqueous NaOH (3.5 mL), and hexane (0.5 mL). The funnel was swirled vigorously and shaken gently, the layers were separated, and the organic layer was dried over anhydrous K_2CO_3 and analyzed by GLC. One chromatogram on a packed column and six–eight chromatograms on a capillary column were run to determine the ratios **4**:DMP and **7**:**8**. For the reaction around room temperature, ten more samples were taken at regular intervals over an 8-h period; then another sample was taken after 24-h reaction time. The sampling times for reactions at other temperatures were chosen depending upon the rate of conversion. Immediately after that, the remainder of the TFA solution was poured slowly into a beaker containing K_2CO_3 (6.27 g), ice–water, and isopentane (5 mL), swirling the beaker gently. The layers were separated, the water layer was extracted with isopentane (4 mL), and the combined isopentane solution was dried over K_2CO_3 and analyzed by GLC. The ratio **7**:**8** was the same in the last 0.5-mL sample taken and in the final quench.

Additions to 5 and 6. The acid (1 mL) was placed in a screwcap test tube which was placed in the thermostated bath at −18 °C. After temperature equilibration, the cap was taken off, and the 1:1 (v:v) mixture of **5** or **6** and DMP (90 μL), taken in a chilled syringe, was injected into the acid, which was quickly swirled, a mixture of 2 N NaOH (6.6 mL), ice, and hexane (0.5 mL) was added rapidly to the test tube. A second operator measured with a stopwatch the time between injection and quenching. Several such runs were conducted, the reaction times varying from 5 to 15 s. Workup and analysis were as above.

The runs in unbuffered TFA, in TFA-*d*, and in 74:26 TFA–MeCN were conducted in the same way as the reactions in buffered TFA, for each alkene, but for **5** and **6** in TFA–MeCN the test tubes were kept capped between reactant addition and quenching.

Determination of Deuterium Distribution in 7 Formed by Addition of TFA-*d* (Buffered) to 3. The mixture of esters was subjected to GC-MS[1a,22] with chemical ionization using isobutane as reagent gas. The deuterium content of each fragment was averaged over the entire GLC peak.[22] Two chromatograms gave (a) m/z 168 = 653, m/z 169 = 6224, m/z 170 = 3188 (**10**/**10**-*d* = 69.0:31.0) and m/z 111 = 1496, m/z 112 = 5920, m/z 113 = 27104, m/z 114 = 44608 (**9**/**9**-*d* = 38.2:61.8); (b) m/z 168 = 456, m/z 169 = 2014, m/z 170 = 1054 (**10**/**10**-*d* = 68.3:31.7) and m/z 111 = 515, m/z 112 = 4128, m/z 113 = 8976, m/z 114 = 19008 (**9**/**9**-*d* = 32.1:67.9). The m/z 111 to 114 group of peaks was also analyzed in two GC-MS runs with EI ionization: (c) m/z 112 = 1885, m/z 113 = 72138, m/z 114 = 12437 (**9**/**9**-*d* = 37.3/62.7); (d) m/z 113 = 34418, m/z 114 = 70360 (**9**/**9**-*d* = 33.3:66.7). Average values: **10**/**10**-*d* = 68.65:31.35 (±0.35); **9**/**9**-*d* = 35.2:64.8 (SD 2.6).

Product Analysis for Reaction of 6 in TFA–MeCN. (a) Formation of 6 from 5. The ratio of **5**/**6** as a function of conversion (initial **5** = 100) in samples from three runs was (A) 61.0/2.3, 48.3/3.2; (B) 34.3/7.0, 18.9/6.9, 13.8/7.9, 10.3/6.4, 4.7/4.7; (C) 33.9/6.7, 16.7/7.8, 9.8/5.9, 6.5/5.8, 4.2/4.6.

(b) Final Quench. The solution obtained from 0.5 mL of **6** and 0.43 mL of DMP after reaction in TFA (9 mL) and MeCN (3.15 mL) at 25 °C for 20 min was quenched in ice–water and K_2CO_3 and extracted with ether. The dried ($MgSO_4$ and K_2CO_3) ether solution was concentrated on an annular column and subjected to capillary GLC. The peaks for **8** and **11** were observed in a 12.6:1 area ratio. The MS of **11** exhibited ions at m/z 129 (vw), 114 (vw), 100 (m), 86 (vw), 72 (m), 71 (w), 70 (w), 60 (m), 58 (vs), 55 (mw), 43 (ms), 42 (m), and 41 (mw), being identical with the spectrum of **11** prepared from 2-methyl-2-butaneamine (20 mmol), acetyl chloride (40 mmol), and NaOH (2 g) in water (10 mL)–ether (35 mL) mixture, at room temperature.

Reaction of 4 in TFA–TsOH. $TsOH\cdot H_2O$ (0.1855 g, 0.976 mmol) was dissolved in 99% TFA (4.1058 g, 36 mmol) and TFA anhydride (1.3293 g, 6.32 mmol) to consume the water from the two acids (the calculated final concentration of anhydride was 0.2%). The acid was cooled to −10 °C and 0.18 mL of a solution of **4** in chloroform (0.385 g **4** per mL) was injected from a syringe. After mixing, part of the solution was transferred to a precooled 8-mm tube fitted inside a 10-mm NMR tube containing deuteriochloroform (lock solvent).[28] The conversion was monitored by ^1H NMR on the olefinic methylene signal of **4** (4.8–5.0 ppm counting the internal $CHCl_3$ as 7.24 ppm), the CHO signal of **3** (4.63 ppm), and the methyl signal of **8** (6H, 1.63 ppm). The duration of a scan (160 pulses) was 5.5 min; therefore the measured half-life for **4** (30 min) is only an approximation. The CHO signal of **7** (5.1 ppm) was too small for accurate integration, but the methyl doublet of **7** at 1.39 ppm (3H) was strong enough for integration.[1a,29] The first spectrum which gave good integration had the alkene more than half converted and showed a **3**/**8** ratio of 0.865. Therefore, the initial **3**/**8** ratio was at least 1, most probably higher.

Exchange of 8 with TFA-*d*. The ester (0.043 g, 0.23 mmol), 2,3-dimethylpentane (0.027 g, 0.27 mmol), and buffered TFA-*d*[1a] (1.5 mL) were kept at 26.4 °C for varying lengths of time, in a test tube with a Teflon-lined screw cap. The nearly colorless solution was poured slowly over a mixture of ice, K_2CO_3 (2.76 g), and isopentane (5 mL). The layers were separated and the aqueous phase was extracted with isopentane (5 mL). The

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[28] Fărcaşiu, D.; Marino, G.; Miller, G.; Kastrup, R. V. *J. Am. Chem. Soc.* **1989**, *111*, 7210.

[29] The chemical shifts in TFA with chloroform as chemical shift standard differ somewhat from the values in deuteriochloroform with internal TMS reported in ref 1a.

combined organic solution was dried (K_2CO_3) and concentrated to 2 mL on an annular column. The D content was seen best in the *m/z* 71 ($C_5H_{11}^+$) fragment in the MS spectrum:

t = 4.77 h: 1.6% d_0, 1.7% d_1, 5.0% d_2, 12.6% d_3, 23.3% d_4, 27.3% d_5, 19.3% d_6, 8.2% d_7, 1.0% d_8

t = 88.5 h: 1.2% d_3, 3.7% d_4, 10.2% d_5, 21.5% d_6, 33.4% d_7, 30.0% d_8

Two exchange experiments at short time gave the following results for deuterium distribution. (a) 132 s, *m/z* 155: 97.2% d_0, 2.4% d_1, 0.5% d_2; *m/z* 169 91.2% d_0, 8.2% d_1, 0.6% d_2. From these values, the ethyl group is 92.5% d_0, 7.2% d_1, 0.3% d_2 (7.8 atoms exchanged out of 200, $k_{exch} = 3.0 \times 10^{-4}\ s^{-1}$) and one methyl group is 98.6% d_0, 1.2% d_1, 0.2% d_2 (1.6 atoms exchanged out of 300, $k_{exch} = 4.05 \times 10^{-5}\ s^{-1}$). The ratio of the two exchange rates is 7.4. (b) 132.5 s, *m/z* 155: 96.9% d_0, 2.8% d_1, 0.4% d_2; *m/z* 169: 86.5% d_0, 12.4% d_1, 1.1% d_2, whence Et 87.9% d_0, 11.4% d_1, 0.8% d_2 (13.0 of 200 atoms exchanged, $k_{exch} = 5.1 \times 10^{-4}\ s^{-1}$), Me 98.4% d_0, 1.4% d_1, 0.2% d_2 (1.8 of 300 atoms exchanged, $k_{exch} = 4.6 \times 10^{-5}\ s^{-1}$). Ratio of exchange rates is 11.1.