Studies in Trifluoromethanesulfonic Acid. 2.[1] Kinetics and Mechanism of Isomerization of Xylenes

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The rates of isomerization of *o*- and *p*-xylenes to *m*-xylene have been measured in the solvent trifluoromethanesulfonic acid (triflic acid, CF_3SO_3H), using NMR, GLC, and conductimetric methods. At low concentration (<0.02 M) the expected first-order kinetics were observed, whereas at higher concentrations the reactions followed apparent second-order kinetics. The mechanism of the reaction is discussed in terms of intimate ion pairing and possible incursion of donor–acceptor complexes between protonated and unprotonated solute molecules.

Introduction

Aromatic compounds in strongly acidic media are protonated to form arenium cations whose stability parallels their basicity.[2] The alkylated aromatics, in particular, undergo very facile protonation in FSO_3H–SO_2 and related systems. Recently, attention has been focused on the use of trifluoromethanesulfonic acid[3] (triflic acid) as a medium for studying such protonation[1] and for promoting electrophilic substitution. A very recent study of the acid as a solvent for conductimetric work[4] revealed that even deactivated aromatics such as nitrobenzene were almost completely protonated (K_b for $C_6H_5NO_2$ = 0.32). In this, and subsequent papers, we report on the structure and mechanisms of various reactions in triflic acid, many of which proceed much more rapidly and cleanly than in other strongly acidic media. This paper describes a study of the mechanism of isomerization of *o*- and *p*-xylenes to the thermodynamically more stable meta derivative.

Results and Discussion

The migration of alkyl groups around an aromatic ring[5] system or from one ring to another (transalkylation) is well-known to be catalyzed by acids.

Both isomerization and transalkylation usually occur together except for R = Me where the free methyl cation has a very low stability. Thus, xylenes can be isomerized in HF–BF_3 mixtures without added complications from intermolecular reactions.[6,7] It was also found that *p*-xylene and *o*-xylene can each be isomerized to *m*-xylene with no direct interconversion of the ortho and para isomers[5,7,8] unlike the di-*tert*-butylbenzenes.[9] Brown[5] reported a detailed kinetic study of the reactions for HBr–$AlBr_3$ in toluene and found that the rate data surprisingly fitted *second-order* rather than the anticipated first-order kinetics. The reactions were very slow and necessitated the use of highly concentrated solutions, a point that will be referred to later. The above reaction media have the disadvantage that handling is difficult and sometimes two-phase systems are formed. Sulfuric acid cannot be used since facile sulfonation of xylenes occurs. Methanesulfonic acid has been used to isomerise tri- and tetramethylated benzenes,[10] but *o*- and *p*-xylenes were found to be inert at the high temperatures (180 °C) used.

Table I. Isomerization of *o*- to *m*-Xylene (0.241 M) in CF_3SO_3H at 25.0 °C [NMR Method (k_1, s^{-1}; k_2 L mol^{-1} s^{-1})]

time, min	A_o[a]	A_m[a]	x/a	$\ln xe/(xe - x)$	10^4k_1	10^4k_2
0						
3	79	2	0.024	0.028	1.56	4.6
15	70	7	0.091	0.112	1.25	4.6
29	64.5	12.5	0.163	0.210	1.21	4.3
41	59	15.5	0.208	0.277	1.13	4.5
60	54	21	0.280	0.393	1.09	4.3
76	50	23.5	0.319	0.463	1.02	4.2
117	43.5	31	0.417	0.662	0.94	4.2
145	38.5	34.5	0.472	0.795	0.91	4.3
∞	10.5	64.5	0.861			

[a] Integrated areas for ortho and meta signals in arbitrary units.

Table II. Isomerization of *o*- to *m*-Xylene (0.241 M) in CF_3SO_3H at 25.0 °C [GLC Method (k_1, s^{-1}; k_2, L mol^{-1} s^{-1})]

time, min	A_o[a]	A_m[a]	x/a	$\ln a/(a - x)$	10^4k_1	10^4k_2
0						
10	663	43	0.061	0.063	1.05	4.5
30	624	124	0.166	0.181	1.01	4.6
53	567	194	0.255	0.294	0.93	4.5
72	534	243	0.313	0.375	0.87	4.4
93.5	492	289	0.370	0.462	0.82	4.4
121	387	283	0.423	0.550	0.76	4.2
149	400	340	0.460	0.616	0.69	4.0
∞	104	736				

[a] Areas of peaks on GLC traces for *o*- and *m*-xylenes in arbitrary units.

Table III. Product Analysis of Equilibration of Xylenes in CF_3SO_3H at 25 °C for 7 Days (% Products)

initial isomer	toluene	xylenes			trimethylbenzenes	
		o	m	p	1,3,5	1,2,4
ortho	1.1	6.4	86.1	5.1	0.7	0.6
meta	2.5	5.1	83.6	6.2	1.8	1.0
para	3.7	4.2	82.3	6.0	2.5	1.3
para[a]	3.6	4.0	83.4	4.5	3.1	1.3

[a] Reaction in CF_3SO_3D.

We have examined the reaction in triflic acid and found that the xylene isomerization ortho → meta and para →

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Table IV. Initial Rates v_0 (mol L^{-1} s^{-1}) and the Dependence of Kinetic Form on Concentration for the Isomerization of *o*- to *m*-Xylene in CF_3SO_3H at 25.0 °C

[*o*-xylene]	$10^5 v_0$	$10^4 k_1$	$10^4 k_2$	r_1[a]	r_2[a]	N[b]
0.00828	0.28	3.9 ± 0.1	*c*	0.999	0.994	6
0.0821	1.4	2.3 ± 0.1	*c*	0.999	0.994	6
0.0207		1.5 ± 0.1	*c*	0.998	0.991	4
0.241	2.9	*c*	4.4 ± 0.2	0.989	0.999	8
0.241[d]		*c*	1.25 ± 0.04	0.996	0.999	6
0.395	3.6	*c*	2.2 ± 0.2	0.990	0.999	7
1.08		*c*	3.4 ± 0.2	0.991	0.998	7

[a] Correlation coefficients for first- and second-order plots. [b] Number of points. [c] Plots curved. [d] In the presence of 0.241 M CF_3SO_3Na.

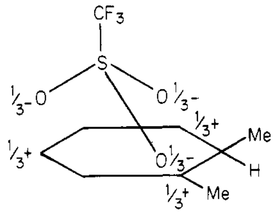
meta proceeds at a conveniently measureable rate at 25 °C in this powerfully acidic medium ($H_0 = -14.6$[11]). Two analytical methods were used.[16] The reaction was followed initially by direct observation of the methyl resonances of the factor and product xylenes (ortho, 1.93; para, 2.00; and meta, 2.47 ppm). Typical data appear in Table I. Subsequently, runs were monitored by quenching in H_2O/CCl_4 mixtures and analyzing CCl_4 layer for xylenes by GLC chromatography (Table II).

No appreciable quantities of disproportionation products were found over a period of 24 h at 25 °C. After 7 days of equilibration, significant amounts of toluene and 1,3,5- and 1,2,4-trimethylbenzenes were detected. Table III lists the yields of the above products. Disproportionation (transalkylation) appears to be greatest for para and least for ortho, though the origin of this effect is not easy to discover. The least stable and hence most reactive protonated xylene is the 1-protonated *m*-xylene. On the other hand, the concentration of unprotonated *m*-xylene will be much lower than those for the other two isomers [pK_B values: ortho, 5.3; para, 5.7; meta, 3.2].[12] The actual yields will therefore depend on a subtle balance of these and other factors such as steric effects for the transalkylation processes. That the principle source of the trimethylbenzenes is via such a route is confirmed by the approximately equal concentrations of these species and toluene found for all three starting isomers.

In CF_3SO_3D experiments a slow exchange of the methyl hydrogens in *m*-xylene was observed. After 19 days, 21% of the protons had been replaced by deuterons.

One of the most striking features of the data in Tables I and II is the systematic decrease of the first-order rate constants with time and the constancy of the *second*-order constants. This result was surprising and accordingly the concentration was decreased over a 30-fold range. The results appear in Table IV. The reactions became *faster* on dilution, the k_1 values becoming constant and the k_2 values variable at <0.02 M. When the reaction was conducted in the presence of sodium triflate, a marked reduction in rate occurred.

One possible explanation of this phenomenon is that at the higher concentrations dimeric species[1] are formed by charge transfer from unprotonated xylene to its conjugate acid, which would give the observed apparent second-order dependence. However, in this medium, the concentration of unprotonated species required for dimer formation would be extremely low. An alternative explanation is that at higher concentrations, intimate ion-pair formation becomes important. We have recently obtained evidence for such species from conductivity and NMR chemical shift data for toluene in CF_3SO_3H.[1] Structure I is attractive since the partial charges on both ions match up to give a favorable electrostatic interaction. It is likely that the proximity of the S–O poles would inhibit a 1,2 migration of the methyl group with its bond pair.



I

The overall protonation–dissociation process can be represented as follows:

$$\mathrm{ArH} + \mathrm{HX} \overset{K_1}{\rightleftharpoons} (\mathrm{ArH_2^+{\cdot}X^-}) \overset{K_2}{\rightleftharpoons} \mathrm{ArH_2^+} + \mathrm{X^-} \quad (1)$$

The concentration of triflic acid (HX) is much greater than the total concentration of aromatic species, $[\mathrm{ArH}]_0$. The concentration of free ions $[\mathrm{ArH_2^+}]$ can then be expressed as a quadratic equation in terms of K_1, K_2, $[\mathrm{ArH}]_0$, and [HX]. The square root part of the solutions to this equation can be expanded as a convergent series provided than $4[\mathrm{ArH}]_0/K_2 < 1$, which in view of the concentrations used in the work is a reasonable assumption. If three terms are taken in the expansion, then:

$$[\mathrm{ArH_2^+}] = a[1 - (a(1 + K_1b)/K_1K_2b)] \quad (2)$$

where $a = [\mathrm{ArH}]_0$, $b = [\mathrm{CF_3SO_3H}]$, and k_1, K_2 are the equilibrium constants for protonation and ion-pair dissociation, respectively. Thus, if I inactivates the isomerization, the overall initial rate of reaction, v_0 is given by:

$$v_0/a = k_1\{1 - [a(1 + K_1b)/K_1K_2b]\} \quad (3)$$

A plot of v_0/a vs. a should give a straight line of negative slope. The data in Table IV give a curve with a negative slope. It is probable that a better approximation would obtain if a further term in the expansion employed in the derivation were taken, leading to a quadratic expression. The fact that added CF_3SO_3Na in equimolar quantities causes a 4-fold decrease in rate appears to support the ion-pair postulate by a common ion effect on equilibria 1. This interpretation must be qualified by the difficulty in assessing ionic strength effects in this medium since any added salt of an acid weaker than triflic acid will always lead to triflate anion formation. Charge-transfer dimers

$$\mathrm{CF_3SO_3H} + \mathrm{NaX} \rightleftarrows \mathrm{CF_3SO_3^-\ Na^+} + \mathrm{HX} \quad (4)$$

do have a real advantage in explaining the quite precise correlation with the second-order kinetic form, whereas the ion-pair formulation results in an intractable rate equation that may fortuitously approximate to apparent simple second-order kinetics. Further, the concentration of unprotonated aromatic will increase with increasing total concentration, making dimerization more plausible. On the other hand, no change in kinetic order was observed for the transalkylation of *m*-diethylbenzene in the same solvent,[13] a reaction in which such complexes should orientate the molecules favorably for reaction. The isomerizations of both *o*- and *p*-xylenes at 0.24 M were run at various temperatures, and the activation parameters were obtained from the k_2 values. The data appears in Table V. Interestingly, for a second-order process the $\Delta S^‡$ values are not very negative. This would support either dimer

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Table V. Variation of Second-Order Rate Constants (k_2, L mol^{-1} s^{-1}) with Temperature (°C) for the Isomerization of *o*- and *p*-Xylenes at 0.241 M

T	24.9	25.3	30.0	35.4	40.7	41.0
10^3k_2(para)	0.48		1.44	2.6	4.7	
10^3k_2(ortho)		0.41	0.66	1.46		2.36

Activation Parameters[a]

	E_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
ortho	21.3 ± 1.3	20.7 ± 1.3	−4.7 ± 4.3
para	20.9 ± 0.3	20.3 ± 0.3	−2.5 ± 0.9

[a] E_a, $\Delta H^{\ddagger}$ in kcal mol^{-1}, $\Delta S^{\ddagger}$ in cal K^{-1} mol^{-1}.

Table VI. Variation of First-Order Rate Constants (k_1, s^{-1}) with Temperature (°C) for the Isomerization of *o*- and *p*-Xylenes at 8.3×10^{-3} M

T	25.3	30.5	35.1	40.0
10^4k_1(ortho)	3.9	6.6	9.8	15.1
10^4k_1(para)	8.9	14.0	21.0	28.7

Activation Parameters[a]

	E_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
ortho	17.1 ± 0.3	16.5 ± 0.3	−18.9 ± 0.9
para	15.0 ± 0.6	14.4 ± 0.6	−24.3 ± 2.1

[a] E_a, $\Delta H^{\ddagger}$ in kcal mol^{-1}, $\Delta S^{\ddagger}$ in cal K^{-1} mol^{-1}.

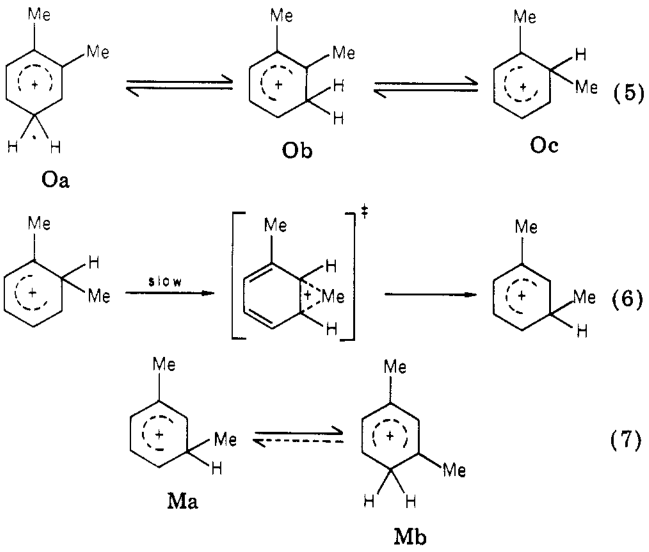
or intimate ion-pair formation in the initial state followed by dissociation of the complexes to allow methyl migration to occur. By working at concentrations <0.02 M, the expected simple first-order rate laws are obeyed accurately. Activation parameters for both ortho to meta and para to meta isomerization were obtained from data at various temperatures (Table VI).

Previous work in HF/SbF$_5$[4] and HBr/AlBr$_3$[5] reported $\Delta H^{\ddagger}$ values of 20–22 kcal mol^{-1} and $\Delta S^{\ddagger}$ values of 0 to −3 cal K^{-1}. For a simple rate-determining 1,2 methyl shift, one would predict values of $\Delta S^{\ddagger}$ close to zero. In HF/BF$_3$[7] large negative $\Delta S^{\ddagger}$ values were obtained, but unfortunately the activation parameters were obtained from data at only two temperatures and substantial errors are probable. In the present work fairly negative values of $\Delta S^{\ddagger}$ were obtained (−19, −24 cal K^{-1} mol^{-1} for *o*- and *p*-xylenes, respectively) and seem at odds with a simple 1,2 methyl shift.

The overall mechanism may be written as shown in Scheme I. Since exchange of the CH$_2$ protons of the xylenium ions with solvent is rapid in CF$_3$SO$_3$H, equilibria 5 and 7 are probably established by deprotonation–deprotonation processes in contrast to the HF–SbF$_5$ system[14] where 1,2 hydride shifts are postulated. The driving force for the reaction comes from the differences in stability of ions Ob and Mb. The latter is calculated[14] to be more stable than the former by about 3 kcal mol^{-1} and is due to the stabilizing influence of both methyl substituents in Mb. Oa and Ob have very similar energies and thus the CH$_2$ protons are highly mobile. Such mobility is lost in the transition state depicted in reaction 6, particularly if the migrating methyl group is half transferred. One cannot completely discount transfer of an incipient methyl cation to one of the oxygen atoms of the triflate anion, the reaction then proceeding by a simple switch process. This obviously could also account for the negative $\Delta S^{\ddagger}$ values, and triflate esters are known to act as alkylating agents.

It is still unclear why in the HF–SbF$_5$ system values are considerably more positive. At the concentrations employed (~0.5 M) it is quite likely that ion pairs are formed by electrostatic interaction between the fluorines and the positive carbon centers.[15] As in the case of the triflate ion pairs, 1,2 methyl and hydride shifts would be inhibited by the proximity of the electric field due to the fluorine poles. Thus the ion pair would have to dissociate before isomerization could occur.

Scheme I



Finally, a brief study of isotope effects was made by comparing runs in CF$_3$SO$_3$H and CF$_3$SO$_3$D. For *o*-xylene a k_H/k_D value of 0.96 was obtained at 25 °C. This value is in keeping with the generally accepted mechanism and certainly precludes any rate-determining proton transfer.

Experimental Section

Trifluoromethanesulfonic acid (3M chemicals) was fractionated twice from a small quantity of P$_2$O$_5$ prior to use. The xylenes (Aldrich Chemical Co., 99% purity) were each dried and fractionated before use. *p*-Xylene-d_{10} (Aldrich Chemical Co., 99+ atom % D) was dried over MgSO$_4$ and used directly.

Kinetic Methods. a. NMR. The appropriate volume of *o*-xylene was injected into 1.00 mL of CF$_3$SO$_3$H at 25 °C by means of a Hamilton syringe and the solution transferred rapidly to an NMR tube, which was then placed in the thermostat bath. The tube was removed from the bath at suitable time intervals, and the NMR spectra were run quickly on a Varian EM 360 spectrophotometer housed in a constant-temperature room with a probe temperature of 28.4 °C. The peaks due to *o*- and *m*-xylene appeared at δ 1.93 and 2.42, respectively, which were integrated in the usual way and the relative concentration of the two species was calculated from a ratio of the integrals (Table I). The ratios were reproducible to about ±5%.

b. Quenching Method. The appropriate volume of xylene was injected into 3.00 mL of CF$_3$SO$_3$H in a thermostat bath and the whole shaken. At suitable time intervals, 0.30-mL aliquots were withdrawn and quenched in a mixture of CCl$_4$ (0.5 mL) and distilled water (1.0 mL) at 0 °C. The upper aqueous layer was drawn off with a Pasteur pipet and the residual CCl$_4$ layer dried with Na$_2$CO$_3$. Samples (3 μL) were analyzed on a Perkin-Elmer F17 chromatograph using a stainless steel column (4 m × 1/8 in.) packed with 5% di-*n*-decylphthalate + 5% Bentone 34 on Chromosorb W (80–100 mesh). The column temperature was 90 °C. The retention times of *o*-, *m*-, and *p*-xylene under these conditions were 21, 18, and 17 min, respectively. Fractions of reaction were calculated from the area ratios on the traces and were reproducible to ±3%. The sum of the areas due to factors and products was constant to within ±3.5% during any one run,

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(16) We have recently found that the reaction can also be followed conductimetrically, since *o*- and *p*-xylenes have substantially lower specific conductances than *m*-xylene.[1] The agreement obtained between this and the other two methods employed are good.

Table VII. Variation of Specific Conductivity κ ($\mathrm{ohm}^{-1}\ \mathrm{cm}^{-1}$) with Time for a Solution of *p*-Xylene in CF_3SO_3H (0.24 M) at 25.3 °C

T, min	0	3	5	10	15	25	35	45	110	120	∞
$10^3\kappa$	1.9	2.2	2.4	3.0	3.5	4.2	4.8	5.0	6.5	6.7	10.1

which indicates that transalkylation reactions are not appreciable over the reaction period (usually ~2 h).

c. Conductivity Method. The appropriate volume of xylene was injected into 2.00 mL of CF_3CO_3H in a small test tube at 25 °C. After shaking, the conductivity of the solution was measured with an LKB-Producter AB Conductolyzer (LKB 5300 A) equipped with a dip cell. The data for *p*-xylene appears in Table VII. The apparent second-order rate constant, k_2, calculated from this data was 9.8×10^{-4} L $\mathrm{mol}^{-1}\ \mathrm{s}^{-1}$, whereas that from the quenching method was 10.3×10^{-4} L $\mathrm{mol}^{-1}\ \mathrm{s}^{-1}$.

Acknowledgment. I thank Ms. H. J. Bakoss for help in the conductimetric work.

Registry No. CF_3SO_3D, 66178-41-4; SbF_5, 7783-70-2; HF, 7664-39-3; CF_3SO_3H, 1493-13-6; H_2, 1333-74-0; HBr, 10035-10-6; $AlBr_3$, 7727-15-3; *o*-xylene, 95-47-6; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; 1,3,5-trimethylbenzene, 108-67-8; 1,2,4-trimethylbenzene, 95-63-6; toluene, 108-88-3; sodium triflate, 2926-30-9.

Studies in Trifluoromethanesulfonic Acid. 3.[1] Kinetics and Mechanism of Transalkylation Reactions

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Rates of disproportionation of ethylbenzene and *m*-diethylbenzene have been measured in the solvent trifluoromethanesulfonic acid (triflic acid). Ethylbenzene disproportionates very rapidly, whereas *m*-diethylbenzene reacts at a conveniently measurable rate. The reactions obey first-order kinetics over a wide range of concentration, and the results are interpreted as involving ethyl transfer to the triflate anion followed by alkylation via the ethyl triflate formed.

Introduction

Transalkylation reactions have long been known in aromatic chemistry and form the basis of important commercial synthetic processes. These reactions are very often accompanied by isomerization of the starting alkyl aromatic to a thermodynamically more stable isomer (e.g., *m*-xylene in the case of *o*- and *p*-xylenes). Transalkylation is usually carried out on an industrial scale, using mordenite or zeolite catalysts at high temperatures. Relatively little work has been done in homogeneous media and it is the purpose of this paper to report on the very facile transalkylations of ethylated benzenes in trifluoromethanesulfonic acid (triflic acid).

Results and Discussion

The mechanism of transalkylation has received a good deal of attention over the years. Early work by Heise and Töhl[2] on the disproportionation of *n*-propylbenzene in an $AlCl_3$–HCl medium at 100 °C showed that the reaction proceeded without rearrangement of the alkyl carbon chain. This work has been confirmed and extended by McCauley and Lien[3] and others, using the same catalytic medium. An S_N2 type of mechanism was suggested to account for this observation.[3] However, the relative rates of various alkylated aromatics varied over a very wide range (Me, 10^{-7}; Et, 1; *i*-Pr, 10^2), which is at odds with the relatively small charge separation implicit on S_N2 process. Brown and Smoot[4] suggested a rapid equilibrium involving a "localized" π complex as an intermediate to account for these relative rates. This mechanism, however, implies that intramolecular isomerization should be much more rapid than transalkylation reactions, which is in conflict with experimental findings.[5–7] Roberts and co-workers[8] have shown that the observed scrambling of labeled carbon in the α and β positions for *n*-propylbenzene (*n*-Prbz) with $AlCl_3$ can be explained in terms of diphenylpropane intermediates. The carbenium ion, formed by dissociation of the *n*-Prbz–$AlCl_3$ complex, abstracts a hydride ion from a second *n*-Prbz and the resulting carbenium ion effects electrophilic substitution on a further substrate molecule.[9]

Streitwieser and Rief[10] studied the kinetics of transalkylation of radiolabeled and optically labeled ethylbenzene in benzene with a galium tribromide–hydrogen bromide catalyst. Unfortunately, reproducibility in the system was poor. The conclusion reached was that a cation chain reaction occurred, probably catalyzed by the carbenium ion derived from HBr addition to styrene (a likely impurity in ethylbenzene). Moore and Wolf[11] have demonstrated from a study of disproportionation and isomerization reactions of ethylbenzene-*1*-^{14}C in $AlBr_3$–HBr that para alkylation is dominant followed by an intramolecular 1,2 shift of an ethyl group to give the thermodynamically most stable isomer. Previous work suffered from problems of reproducibility caused by inhomogeneous reaction media. It is significant that very few attempts have been made to determine the order of the reaction components. Triflic acid, CF_3SO_3H, has the great advantage of providing a homogeneous medium of high acidity and is much more easily handled than the usual Friedel–Crafts catalytic mixtures.

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