12572 *J. Am. Chem. Soc.* **1996,** *118,* 12572−12579

The First Unequivocal Evidence of the Reacting Electrophile in Aromatic Acylation Reactions[1]

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Received July 15, 1996[⊗]

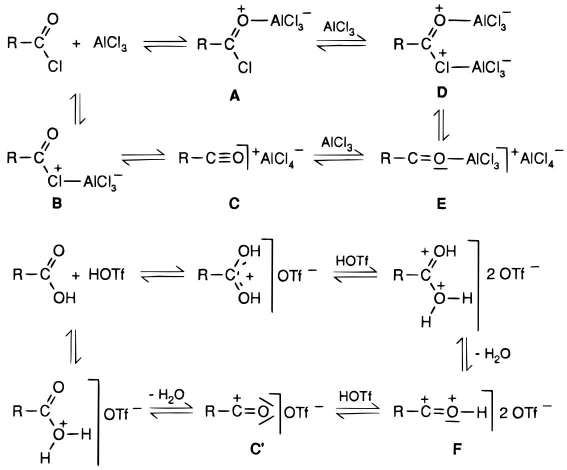
Abstract: The acylation of aromatic compounds with aroyl triflates can be performed in organic solvents (1,2-dichloroethane) without Friedel−Crafts catalysts. These reaction conditions allow kinetic investigations of the reaction in homogeneous solution. From rate measurements evidence is given that in all cases the aroyl triflates **1**, **6**, and **11** dissociate primarily into the corresponding acylium ions which subsequently react with the aromatic compounds. The rate-determining step, either the dissociation of the aroyl triflates or the reaction of the acylium ions with the aromatic, can be assigned definitely from the experimental data. From the kinetic measurements in the presence of an excess of base unequivocal evidence of acylium ions as the reacting electrophiles in all cases investigated is given.

Introduction

The Friedel−Crafts acylation of aromatic compounds is one of the most important reactions in organic chemistry.[3] While there is no doubt that it follows the well-known σ-complex mechanism of electrophilic aromatic substitution,[4] the nature of the attacking electrophile is controversial. Scheme 1 summarizes the possible electrophiles of a mixture of acid chlorides with Lewis acids like $AlCl_3$[5,6] as well as the possible electrophiles of carboxylic acids with strong Brønsted acids.[6]

The oxonium complex **A**[5a,7] and the acylium salt **C**[5b] could be deduced from IR, NMR, and X-ray investigations, while halogen exchange reactions indicate the existence of the adduct **B**.[8] Both ^1H NMR spectroscopic[9] and kinetic studies[10] permit an assignment of the twofold coordinated complex **D**. The significantly high reactivity of $RCOCl{\cdot}2AlCl_3$ complexes is referred to the formation of the complexed acylium ion **E**.[11]

Scheme 1



Acylium ions **C** or **C′** are relatively weak electrophiles which, as stated by Olah,[6] do not react with deactivated aromatics. An activation of acylium ions could be reached, however, either by addition of a second mole Lewis acid to **C** to give complex **E** or in superacidic media by protonation of **C′** resulting in the dicationic species **F** (Scheme 1). The existence of such dications is based on experimental data as well as on theoretical calculations.[12,13]

Protonated acylium ions **F** are proposed to be the reacting electrophiles in the acylation of benzene, toluene and chlorobenzene in superacidic systems.[6,14a,b] The increase of isolated yields of acylation products with raising acid strength (CF_3SO_3H/SbF_5)[14a,b] can be explained by an increasing concentration of protonated acylium ions **F** in the reaction mixture.

Dicationic species are also suggested to be the attacking electrophiles in Friedel−Crafts reactions of benzene with

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[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1996.

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S0002-7863(96)02433-X CCC: $12.00

benzaldehyde,[14c,d] in the Gattermann formylation as well as in the Houben−Hoesch synthesis.[14a,b]

These results obtained in superacidic media, however, cannot be applied unrestricted to the acylation reactions in organic solvents. Depending on the reaction conditions, kinetic studies resulted in different rate laws concerning the Friedel−Crafts catalyst. The respective aromatic compound is always involved in the rate-determining step.

Since Lewis acids, e.g., $AlCl_3$, are only poorly soluble in organic solvents, their concentration cannot be varied independently since normally a heterogeneous reaction system results. A second-order rate law (eq 1) was observed by using acid chlorides as solvent.[15]

$$v = k_2[\mathrm{RCOCl{\cdot}AlCl_3}][\mathrm{ArH}] \quad \text{with } k_2 = \text{const.} \qquad (1)$$

Otherwise (e.g., in DCE) an increase of the rate constant k_2 with the concentration of Lewis acid was observed.[16] Therefore a rate law as a combination of a reaction of first and a reaction of second order refering to the acylation agent was proposed.[10b]

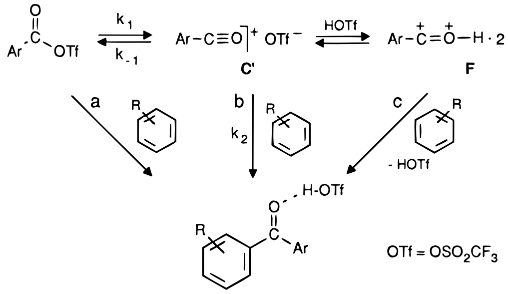
Using the weaker Lewis acids $FeCl_3$, $GaCl_3$ or $SbCl_5$, the situation is even more complex. The reactions follow second-order kinetics refering to the Lewis acid and the rate constants are inversely proportional to the starting concentration of Lewis acid.[17] Recently a fourth-order rate law refering to the Lewis acid $FeCl_3$ in nitromethane as solvent was measured,[18] where the formation of 1:1 and 1:2 ketone-$FeCl_3$-complexes have been included in the rate law.

In order to explain the complexity of the kinetic results of Friedel−Crafts acylations, the various possibilities of complex formation with the acid chlorides,[10,17] the ketones formed[18] and moreover the solvent have to be considered.[19] For this reason of complexity, kinetic measurements of Friedel−Crafts acylations with other carboxylic acid derivatives, e.g., carboxylic acid anhydrides, are hardly described.

It is stated, that the kinetic data available do not allow an unambiguous evidence of the reacting electrophile.[20] Further, it is noted that the mechanistic concepts deduced from kinetic studies could only be falsified but not verified.[21] Thus the rate law in eq 1 gives no real evidence of the type of the reacting electrophile (see Scheme 1).

The interpretation of the mechanism of the Friedel−Crafts acylation with the spectroscopic evidence of intermediates in the reaction mixture is difficult, since all the possible electrophiles exist in an equilibrium (Scheme 1).[22] The spectroscopic detection of single species in the reaction mixture does not allow a prediction of their participation in the reaction.[19] For an exact description of the reaction mechanism a defined acylation agent is required, whose change of concentration can be followed and whose acylation potential is not changed during the reaction, e.g., by formed strong acid.

Scheme 2



Mixed carboxylic trifluoromethanesulfonic anhydrides should be most suitable as clearly defined acylating electrophiles.[23a,b] Benzoyl triflates, for example, dissociate without a catalyst in organic solvents to give acylium ions of type **C′**.[23c] The dissociation equilibrium depends mainly on the structure of the respective carboxylic acid but to a certain extend also on the acidity of the medium.[23c] Besides electron-donating groups in *para-* and *ortho*-position and bulky substituents in *ortho*-position to the carboxylic group,[23c] the addition of trifluoromethanesulfonic acid (HOTf)[23d] favors the dissociation of aroyl triflates.

Scheme 2 illustrates the three possible pathways for the acylation of aromatic compounds with aroyl triflates. If one is able to follow the dissociation of benzoyl triflates experimentally, to remove the strong acid released during the reaction, and to show that undissociated aroyl triflates are not acting as electrophiles it should be possible to carry out acylations of aromatic compounds which proceed unambiguously via the defined electrophile **C′**.

In the present publication we describe kinetic measurements of aromatic acylations with benzoyl triflates where the concentration of acylium ions can be measured and followed by IR spectroscopy. We further demonstrate that undissociated aroyl triflates are not reactive enough to acylate even strongly activated aromatics.

Results and Discussion

Competitive Acylations of Benzene Derivatives with Benzoyl Triflates. In a previous paper[23c] we could demonstrate that aromatic compounds are acylated by carboxylic trifluoromethanesulfonic anhydrides (acyl triflates) without the addition of Friedel−Crafts catalysts. The acylation of benzene with benzoyl triflates resulted in the following reactivity order:[23c] 4-methylbenzoyl < 2,4-dimethylbenzoyl < benzoyl < 2-methylbenzoyl < 4-chlorobenzoyl < 4-nitrobenzoyl.

According to Scheme 2 these experimental results can be explained as follows: in the acylation of aromatic compounds with benzoyl triflates both the dissociation step (k_1/k_{-1}) to acylium ions **C′** as well as the reaction of acylium ions **C′** with the aromatic compound (k_2) can be rate-determining.

The dissociation (k_1 in Scheme 2) of benzoyl triflates to give acylium ions **C′** is favored electronically by donor substituents in *para-* and *ortho*-position and sterically by bulky groups in *ortho*-position to the carboxylic group.[23b] On the other side, the electrophilic potential of all possible electrophiles − the undissociated aroyl triflates, aroylium ions **C′** or **F** − and thus

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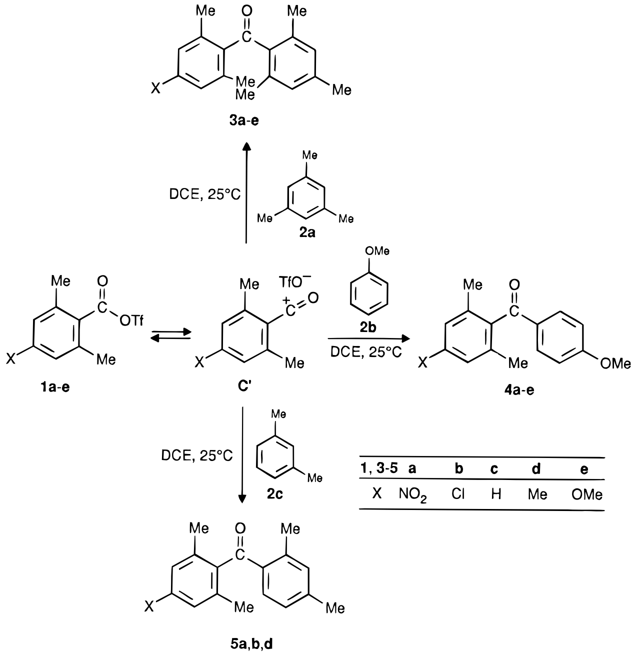
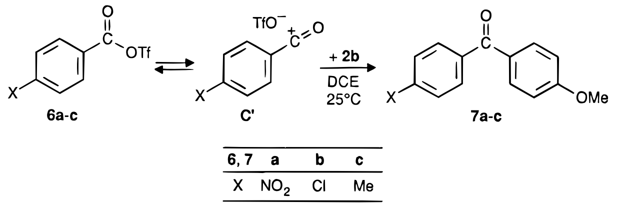
Scheme 3



1, 3-5	a	b	c	d	e
X	NO_2	Cl	H	Me	OMe

Scheme 4



6, 7	a	b	c
X	NO_2	Cl	Me

k_2 in Scheme 2 is increased by electron-withdrawing groups in the aroyl group (4-CH_3 < 4-H < 4-Cl < 4-NO_2).

The dependence of the dissociation equilibrium of benzoyl triflates on electronic and steric factors was determined previously.[23b] The influence of the degree of dissociation on the rate of acylations, however, has not yet been studied. Also the electronic influence of substituents in acylium ions **C′** on reaction rates has so far only been estimated.[23c]

We have now determined the relative reaction rates of the substituted benzoic trifluoromethanesulfonic anhydrides **1a**−**e** and **6a**−**c** with the aromatics **2a**, **2b** and **2c**, respectively, by competitive reactions (Schemes 3 and 4). We have also investigated the selectivity of acylations of several anhydrides **1** toward aromatics of varying reactivity in order to obtain a reactivity−selectivity relation. All investigations were carried out in 1,2-dichloroethane (DCE) at room temperature without addition of Friedel−Crafts catalysts or Brønsted acids. The relative reactivities are independent on the reaction time. They are based on GC fractionation of the derivatized reactants and products.

Figure 1 shows the relative rate constants for acylations of mesitylene (**2a**) with *para*-substituted 2,6-dimethylbenzoyl triflates **1a**−**e** (Scheme 3). From the results shown in Figure 1 one may conclude that the dissociation of 2,6-dimethyl-substituted anhydrides **1a**−**e** to **C′** occurs in a preceding equilibrium. The reaction of acylium ions **C′** with the sterically demanding **2a** therefore becomes rate-determining. The positive ρ-value could be due to the reaction of acylium ions as well as undissociated anhydrides (Scheme 2, path b, a). The clear deviation of the relative rate constant for **1a** indicates that the formation of the corresponding acylium ion **C′** is suppressed by the strong −M-effect of the nitro group and therefore dissociation (k_1/k_{-1}) becomes rate-determining in this case.

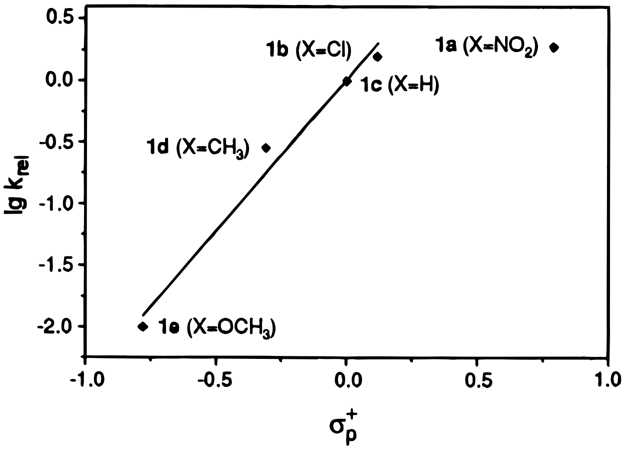


Figure 1. Relative rate constants k_{rel} of the acylation of mesitylene (**2a**) with 2,6-dimethylbenzoyl triflates **1a**−**e** in 1,2-dichloroethane at room temperature.

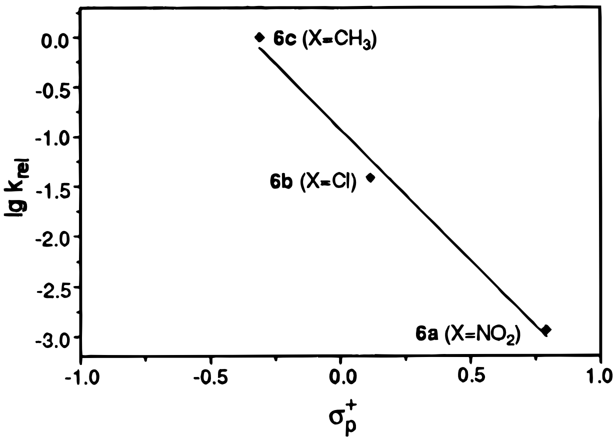


Figure 2. Relative rate constants k_{rel} of the acylation of anisole (**2b**) with benzoyl triflates **6a**−**c** in 1,2-dichloroethane at room temperature.

On the contrary, as seen in Figure 2, in the acylation of the more reactive and less sterically hindered anisole (**2b**) (Scheme 4) the dissociation of the benzoyl triflates **6a-c** becomes rate-determining in all cases and causes an inversion of the reactivity order of the substituted anhydrides.

In order to confirm the change of the rate-determining step in the reactions of anhydrides **1** and **6**, respectively, the rate of the second step (k_2) was systematically varied by changing the reactivity of the aromatics (Figures 3 and 4).

Figure 3 shows a positive ρ-value for the acylation of the less reactive *m*-xylene (**2c**) with the triflates **1a**,**b**,**d**. In this case—in contrary to the reaction with **2a**—also the relative rate for the nitro compound **1a** does not deviate. It can therefore be concluded that in the reaction with **2c** in all cases k_2 is rate-determining. In the reaction of the anhydrides **1a**−**e** with the more reactive anisole (**2b**) (Scheme 3), however, the dissociation of the acceptor substituted and therefore less dissociated anhydrides **1a**,**b** becomes rate-determining whereas for the donor substituted anhydrides **1d**,**e** the reaction of the electrophile **C′** with **2b** (k_2) remains rate-determining. Figure 4 excellently illustrates this change of the rate-determining step depending on the stabilization of **C′** by substituents.

The selectivity of the benzoyl triflates **1a**−**e** in acylations was studied by competitive reactions with **2a** and **2b** (Scheme 3, Figure 5). Figure 5 shows no deviation for the reaction of

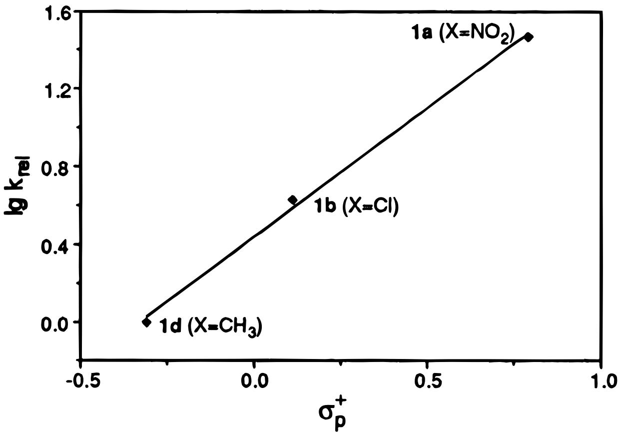


Figure 3. Relative rate constants k_{rel} of the acylation of *m*-xylene (**2c**) with **1a**,**b**,**d** in 1,2-dichloroethane at room temperature.

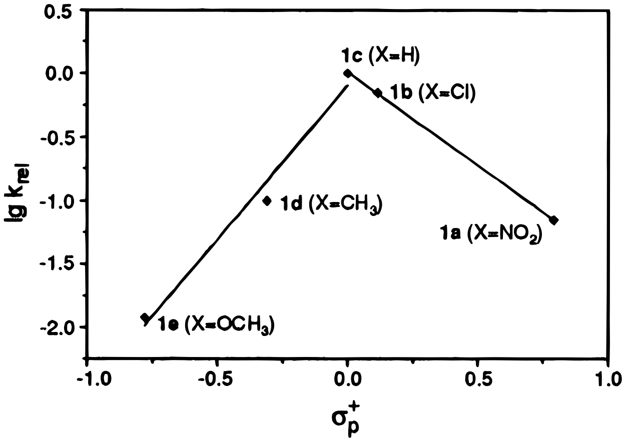


Figure 4. Relative rate constants k_{rel} of the acylations of anisole (**2b**) with **1a**–**e** in 1,2-dichloroethane at room temperature.

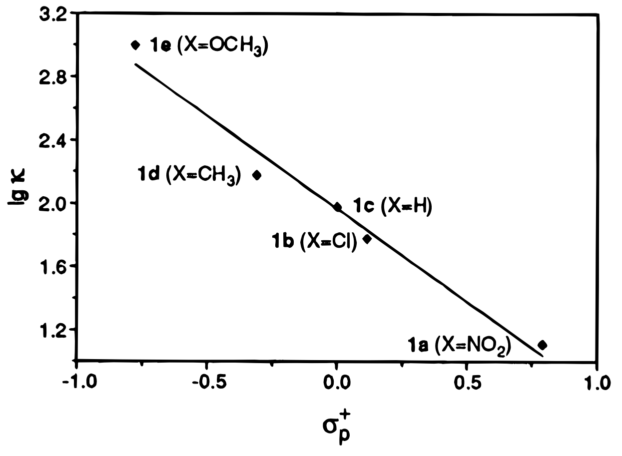


Figure 5. Selectivity κ of competitive reactions of the anhydrides **1a**–**e** with mesitylene (**2a**) and anisole (**2b**), respectively ($\kappa = k_{2b}/k_{2a}$).

1a and therefore a comparable mechanism for the acylation of **2a** and **2b** with **1a** is to be assumed. Figure 6 summarizes the reactivity–selectivity relation for the reactions of anhydrides **1a**–**e**. With the exception of **1a** (compare Figure 1), the correlation of selectivity κ with relative reactivities in the acylation of **2a** corresponds well for the benzoyl triflates **1**.

Based on the experimentally observed data we postulate, that compounds **2a**–**c** were acylated with the anhydrides **1** and **6** via primary dissociation to acylium ions **C′** (Scheme 2, path b and/or path c). The obtained negative ρ-values in Figure 2 and 4 do not correlate with the electrophilic attack of an undissociated anhydride (path a).

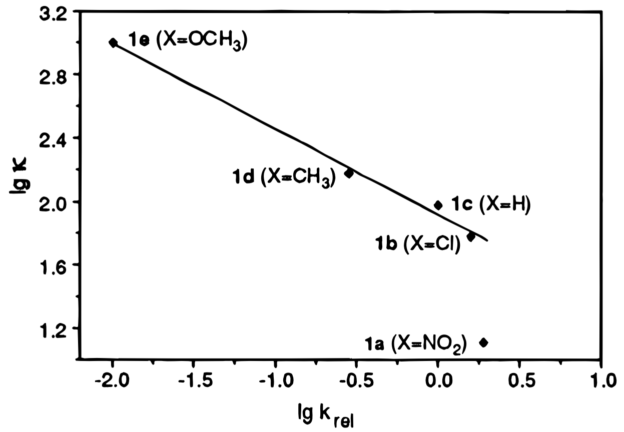
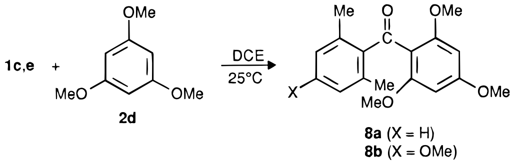


Figure 6. Reactivity–selectivity relation for the anhydrides **1a**–**e**; reactivity k_{rel} based on the acylation of **2a**.

Scheme 5



In order to exclude definitely undissociated triflates **1** or **6** as attacking electrophiles, the very reactive 1,3,5-trimethoxybenzene (**2d**) was acylated with **1c** and **1e** (Scheme 5). Since the donor substituted **1e** reacts faster than **1c** (product ratio **1e**:**1c** = 2.4:1) path a in Scheme 2 can be suspended for the acylation with benzoyl triflates.

Kinetic Studies of the Acylation of Aromatics with Benzoyl Triflate 11b in the Presence of Base. The results discussed so far allow conclusions about the reacting electrophile in acylations of aromatics with aroyl triflates in organic solvents, but they do not consider the role of HOTf released in the acylation, and also the concentration of acylium ions **C′** could not directly be followed during the reaction.

The dissociation of anhydrides **1**, as mentioned above, is influenced by HOTf[23c] and, on the other hand, the reactivity of acylium ions **C′** could be changed by protonation to give **F** (Scheme 2). Both the acylation in presence of a base for removal of the acid released and the use of structurally optimized benzoyl triflates where a direct measurement of the concentration of acylium ions **C′** is possible, should give clear evidence on the acylation mechanism.

For removal of HOTf we have used 2,4,6-tri-*tert*-butylpyridine (**13**)[24] as proton selective base. **13** does not react with benzoyl triflates at room temperature for steric reasons. For following the concentration of acylium ions during the reaction, IR spectroscopy offers the best method.[5b]

In previous investigations[25] we have found that an alkoxy group like the acid-stable neopentyl group in *para*-position and a methyl group in *ortho*-position of the carboxyl group are necessary to get high enough concentrations of acylium ions for kinetic measurements by IR spectroscopy.

As outlined in Scheme 6 we have first prepared 4-(2,2-dimethylpropoxy)-2-methylbenzoyl triflate **11a** as a model compound that dissociates in a 69 mM solution in 1,2-DCE to 1.5% at 25 ± 0.2 °C in the presence of **13**. Further substituents in *ortho*-position, which would increase the dissociation, were not introduced. Starting from methylphenols **9** the triflates **11**

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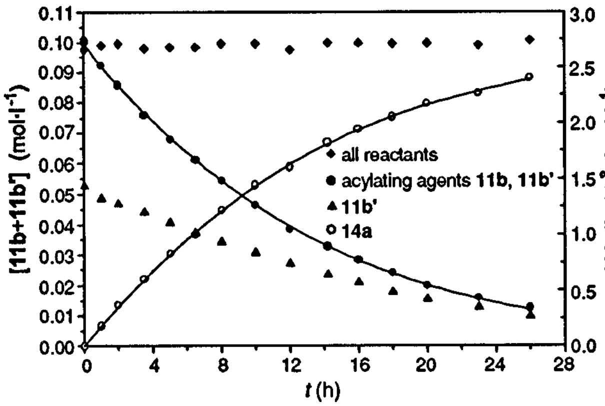
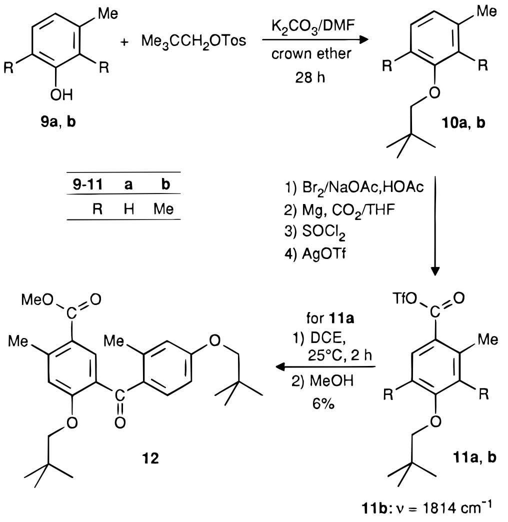


Figure 7. Concentration profiles of **11b**, **11b′**, and **14a** as well as mass balance in the reaction with *p*-xylene (**2e**).

Scheme 6



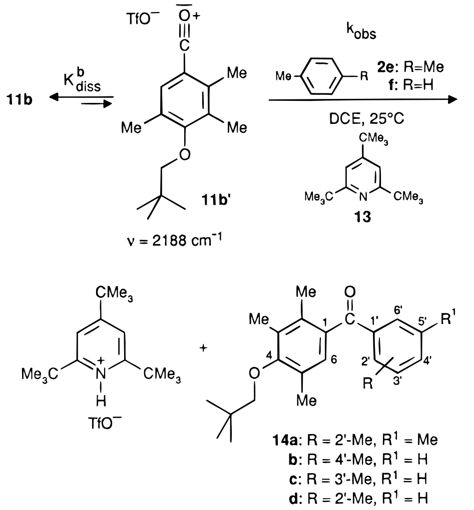
were obtained quantitatively via the corresponding acid chlorides (Scheme 6) according to the method described for compounds **1** and **6**.[23b]

Generally benzoyl triflates are relatively stable in the absence of moisture. The weakly dissociating anhydrides can even be distilled.[23b] Solutions of triflate **11a** in 1,2-DCE, however, are not stable at room temperature, they react by themselves to give oligomeric ketones. Besides numerous not identified products the monobenzoylated derivative which can be isolated as methyl ester **12** is formed within a few hours from **11a** (Scheme 6). **11a** therefore could not be isolated or characterized in pure form.

By introducing further methyl groups in 3- and 5-positions of **11a** the formation of oligomers can be prevented. The triflate **11b**, for example, is stable and was isolated in analytically pure form. HOTf was added to solutions of **11b** to get complete dissociation to the acylium salt **11b′** (Scheme 7). The extinction coefficient of the carbonyl stretching vibration of **11b′** at $\nu = 2188\ \mathrm{cm}^{-1}$ amounts to 117 ± 4 L/mol·cm. We have developed a method to follow the concentration of **11b′** also in the presence of base **13** by IR spectroscopy. For kinetic studies the extremely hygroscopic triflates **11** were prepared in situ.

Kinetic of Reactions of 11b with Aromatics in the Presence of Base 13. Triflate **11b** is reactive enough to acylate moderate activated aromatics at room temperature within a few hours. Due to the favorable reaction rate, *p*-xylene (**2e**) and toluene (**2f**) were reacted with **11b** in the presence of base **13** (Scheme 7). Besides the concentration of acylium ion **11b′** the concentrations of the starting **11b** and the products **14** were followed by gas chromatography after esterification of **11b** with methanol. It was possible to follow the reactions up to a conversion of 50−80% where side reactions did not occur as proved by the mass balance. Figure 7 illustrates as one example the concentration profile of reactants in the acylation of **2e** ($c = 324.4$ mM) with **11b** ($c = 99.9$ mM). The concentration time data were evaluated according to the differential second-order rate law given in eq (2).

Scheme 7



$$v = k[\mathbf{11b'}][\mathrm{ArH}] \qquad (2)$$

The rate constants determined from initial velocities k^{b}_{obs} (start) as well as the averaged rate constants k^{b}_{obs} (average) from the acylation of **2e** and **2f**, respectively, are listed in Table 1. Typical kinetic traces for determination of k^{b}_{obs} (average) are given in Figure 8. The scattering of measuring points is referred to the method of determination of v. As can be seen from Table 1, however, the rate constants resemble with varying concentrations of acylium ion **11b′**. The obtained values of k_{obs} show the higher reactivity of **2e** ($k_{obs} = 4.36 \pm 0.20 \times 10^{-3}$ L/mol·s) compared with **2f** ($k_{obs} = 1.44 \pm 0.20 \times 10^{-3}$ L/mol·s) in acylation reactions. This result correlates with the literature.[10a,15b,c,16a]

It must be noted that the dissociation of **11b** to acylium ion **11b′** could not be incorporated in the evaluation since the dissociation step could not be described simply by, e.g., the formation of an ion pair. Based on the rate law (eq 3) different rate constants k'_{obs} ($k'_{obs} = K^{b}_{diss} \cdot k_{obs}$) (Scheme 7) are therefore obtained.

$$v = k'_{obs}\,[\mathbf{11b}][\mathrm{ArH}] \qquad (3)$$

The evaluation via the integrated rate law was not possible. The calculated values of k_{obs} (Table 1) confirm, however, that the second-order rate law is obeyed.

Rate Constants of the Reaction of 11b with Aromatics in the Presence of HOTf. In the presence of strong acids, acylium ions **C′** could be protonated to **F** (Scheme 1). If a species **F** would contribute decisive to the acylation reaction (Scheme 2), the addition of HOTf should give higher reaction rates than in presence of a base if the formation of a σ-complex is rate-determining.

We have therefore investigated the kinetic of acylations with **11b** adding >150 mol% HOTf. Under these conditions **11b** is

Table 1. Second-Order Rate Constants k^{b}_{obs} of the Conversion of Acylium Ion **11b′** with Compounds **2e**,**f** in the Presence of Base **13** at 25 ± 0.2 °C in 1,2-Dichloroethane

v_{start} mol/L·s·10^{-6}	[**11b**] mol/L·10^3	[**11b′**] mol/L·10^3	[**13**] mol/L·10^3	**2**	[**2e**], [**2f**] mol/L·10^3	k^{b}_{obs} (start) L/mol·s·10^{-3}	k^{b}_{obs} (average) L/mol·s·10^{-3}
1.10 ± 0.02	99.9 ± 0.6	1.67	188	**2e**	162.2	4.06	4.39 ± 0.12
1.90 ± 0.01	99.2 ± 1.0	1.44	188.3	**2e**	324.4	4.07	4.41 ± 0.11
2.28 ± 0.14	124.0 ± 1.6	1.63	200	**2e**	340.0	4.11	4.43 ± 0.21
2.93 ± 0.06	177.2 ± 1.3	2.22	310.7	**2e**	324.4	4.07	4.48 ± 0.19
3.29 ± 0.07	208.8 ± 1.3	2.52	376.3	**2e**	324.4	4.02	4.09 ± 0.14
7.85 ± 0.12	138.6 ± 1.5	1.70	247	**2f**	374	1.23	1.49 ± 0.21
6.46 ± 0.04	93.2 ± 1.7	1.39	150	**2f**	374	1.24	1.39 ± 0.18

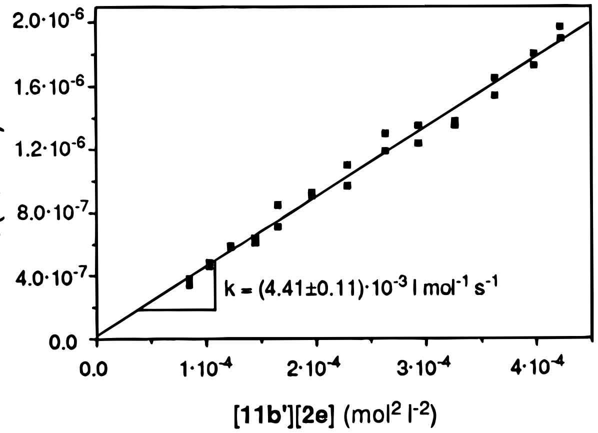


Figure 8. Exemplary evaluation of experimental data to determine k_{obs}.

Table 2. Second-Order Rate Constants k^{a}_{obs} of the Conversion of Acylium Ion **11b′** with Compounds **2e**,**f** in the Presence of HOTf at 25 ± 0.2 °C in 1,2-Dichloroethane

[HOTf] mol/ L·10^3	[**11b′**] mol/ L·10^3	**2**	[**2e**], [**2f**] mol/ L·10^3	k^{a}_{obs} L/ mol·s·10^{-4}	[HOTf]/ [**11b′**]	conv. (%)	*R* value
146	76.4 ± 1.3	**2e**	162.4	4.21 ± 0.07	1.91	50	0.9979
105	61.6 ± 1.3	**2e**	324.8	4.66 ± 0.09	1.70	80	0.9989
107	77.0 ± 1.0	**2e**	162.4	5.77 ± 0.04	1.39	83	0.9995
137	67.0 ± 1.5	**2f**	374.0	2.55 ± 0.05	2.04	51	0.9979
141	75.0 ± 1.5	**2f**	374.0	2.91 ± 0.07	1.88	50	0.9971
129	85.2 ± 2.0	**2f**	374.0	3.36 ± 0.07	1.51	84	0.9973

completely dissociated to **11b′**. Table 2 summarizes the rate constants k^{a}_{obs} at 25 ± 0.2 °C in 1,2-DCE calculated via the integrated second-order rate law based on gas chromatographically determined concentration time data. As seen from the R-values and standard deviations in Table 2 the experimental data are in good agreement with the second-order rate law. The evaluation of acylations of **2e** with **11b′** including the concentrations of **11b′** and of the product is given in Figure 9 as an example. In the presence of the pyridine **13**, compound **2e** is more reactive than **2f**, but in presence of HOTf the difference in rates decreases from ca. 3 to 2.3−1.25.

A comparison of Tables 1 and 2 shows that in the presence of HOTf the rate constant k_{obs} relative to the reactive electrophile of type **C′** is by a factor 5−10 lower than in the presence of base **13**. Moreover the rate constants depend on the reaction conditions: an increase of k^{a}_{obs} is observed either by decreasing the initial concentration of HOTf or by raising the initial concentration of **11b** (Table 2). Thus the second-order rate constant decreases with increasing excess of acid HOTf (Figure 9). These experimental data are a clear evidence against protonated acylium ions **F** as attacking electrophiles in these acylation reactions.

For the decrease of the reaction rates by adding HOTf, on the basis of the pK_a values of −21 for **2f**[26] and −14.1 for HOTf[27] as well as the results described by Farcasiu,[27] we exclude a protonation of the aromatic compound.

Experimental Section

General Methods. Melting points were determined on a Büchi SMP 20 and are uncorrected. ^{1}H NMR spectra were recorded on a Varian T 60 or EM 360 (60 MHz) and a Bruker AC 250 F (250 MHz) in $CDCl_3$ as solvent and TMS as internal standard. FT-IR spectra were recorded on a Bruker IFS 66 v with CaF_2 cuvette (d∼0.1 cm). Gas chromatography: relative reaction rates were determined using a Hewlett-Packard 5710 A with FID, 30 mL/min nitrogen, glass column 2.3 m × 2 mm, phase OV25 or 101 on Gaschrom Q, temperature program: 100 °C, heating rate 16°/min, 300 °C end temperature. For kinetic experiments a Carlo Erba Fractovap 4160 with FID and on column injector was used, 0.45 bar hydrogen, column 20 m, phases PS086 or SDPE08, temperature program: 40 °C isotherm 1 min, heating rate 10 °C/min, 300 °C end temperature. Preparative column chromatography was performed using glass columns of different size, packed with silica gel S, grain size 0.032−0.063 mm (Riedel-de Haen). 1,1,2-Trichlorotrifluoroethane was distilled twice from P_2O_5 under Ar; 1,2-dichloroethane (DCE) was purified as described in the literature[28] but freshly distilled under Ar from CaH_2. Mesitylene (**2a**), anisole (**2b**), and *m*-xylene (**2c**) were distilled and stored over molecular sieve 4 Å. 1,3,5-Trimethoxybenzene (**2d**) was dried over P_2O_5. *p*-Xylene (**2e**) and toluene (**2f**) were distilled over a Spaltrohr column, dried (CaH_2) and freshly distilled. Trifluoromethanesulfonic acid (3 M) was twice fractionally distilled. Tri-*tert*-butylpyridine (**13**) was prepared according to ref 29, recrystallized from MeOH, and dried over P_2O_5. Known (**3c**,**d**,**4b**−**e**,**5d**,**7**)[30] and undescribed diarylketones **3**−**5**,**8** and **14a** were prepared from the corresponding triflates according to ref 23c. The methyl esters were prepared according to ref 31, and triflates **1** and **6** according to ref 23c.

All reactions of **1**,**6** were carried out under exclusion of moisture (P_2O_5 tube) in dried glassware. Experiments with triflates **11** were performed in dry argon atmosphere using Schlenk technique. The apparatus used for kinetic experiments were dried additionally at 250 °C for 2 h; all solids were weighed in a glovebox (MBraun, Inertgassystem MB 150 B-6-l, inert gas Ar 4.6) with a water content <10 ppm, transferred to the apparatus under Ar, and the solutions were added via N_2 dried syringe.

1-(2,2-Dimethylpropoxy)methylbenzenes 10 were prepared according to ref 32. A solution of **9** [66 g, 0.611 mol (**9a**), 36 g, 0.265 mol (**9b**)], K_2CO_3 (80 g, 0.336 mol for **9a**, 36.6 g, 0.265 mol for **9b**), 2,2-dimethylpropyl *p*-toluenesulfonate[33] (72 g, 0.297 mol for **9a**, 53.4 g, 0.220 mol for **9b**), and dibenzo-18-crown-6 (4.0 g, 11 mmol) in dimethylformamide (600 mL) was refluxed for 21−28 h (TLC control). The reaction mixture was cooled to room temperature, diluted with water (1:1), and extracted four times with diethyl ether. The combined extracts were washed with KOH solution and water and dried ($MgSO_4$). After removal of the solvent tarry byproducts were separated by flash chromatography on silica gel with petroleum ether. Distillation yielded 32.6 g (61%) of **10a** and 18.8 g (37%) of **10b** as colorless oils; bp 110 °C/8 Torr (**10a**), bp 123 °C/11 Torr (**10b**). Data see Table 3.

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(26) Marziano, N. C.; Tortato, C.; Bertani, R. *J. Chem. Soc., Perkin Trans 2* **1992**, 955−957.

(27) Farcasiu, D.; Miller, G. *J. Phys. Org. Chem.* **1989**, *2*, 425−427.

Table 3. ^{1}H NMR Data and Elemental Analysis of Compounds **3**−**5**, **8**, **10**−**12**, and **14** as well as Methyl Ester of Triflates **1b** and **11** in $CDCl_3$ at 60 and 250 MHz[a]

	alkyl	
compd	CH_3 (s), OCH_3 (s), CH_2 (s)	phenyl
3a	2.18 (6 H, 2′-,6′-CH_3), 2.28 (6 H, 2-,6-CH_3), 2.33 (4′-CH_3)	6.93 (s, 2 H, H3′,5′), 7.94 (s, 2 H, H3,5)
3b	2.17 (12 H, CH_3), 2.32 (3 H)	6.91 (s, 2 H, H3′,5′), 7.09 (s, 2 H, H3,5)
3e	2.17 (12 H, CH_3), 2.31 (3 H), 3.84 (3 H, OCH_3)	6.63 (s, 2 H, H3,5), 6.91 (s, 2 H, H3′,5′)
4a	2.25 (6 H, CH_3), 3.90 (3 H, OCH_3)	6.90−7.94 (m, 4 H, H2′,3′,5′,6′), 7.95 (s, 2 H, H3,5)
5a	2.27 (6 H, CH_3), 2.40 (4′-CH_3), 2.74 (3 H, 2′-CH_3)	6.99−7.36 (m, 3 H, H3′,5′,6′), 8.01 (s, 2 H, H3,5)
5b	2.12 (6 H, CH_3), 2.36 (3 H, 4′-CH_3), 2.69 (3 H, 2′-CH_3)	7.11 (s, 2 H, H3,5), 6.93−7.35 (m, 3 H, H3′,5′,6′)
8a	2.20 (6 H, CH_3), 3.64 (6 H, 2′-,6′-OCH_3), 3.81 (3 H, 4′-OCH_3)	6.11 (s, 2 H, H3′,5′), 6.83−7.26 (m, 3 H, H3,4,5)
8b	2.20 (6 H, CH_3), 3.90 (6 H, 2′-,6′-OCH_3), 3.77, 3.82 (OCH_3 each)	6.12 (s, 2 H, H3′,5′), 6.53 (s, 2 H, H3,5)
10a	1.03 (9 H, $C(CH_3)_3$), 2.32 (3H), 3.57 (2 H)	6.70−6.80 (m, 3 H, H2,4,6), 7.10−7.25 (m, 1 H, H5)
10b	1.10 (9 H, $C(CH_3)_3$), 2.17, 2.22, 2.24 (3 H each), 3.36 (2 H)	6.81 (AB system, J_o = 7.6 Hz, 1 H, H4), 6.90 (AB system, 1 H, H5)
11b	1.12 (9 H, $C(CH_3)_3$), 2.27, 2.31, 2.53 (3 H each), 3.42 (2 H)	7.71 (s, 1 H, H6)
12	0.68 (9 H), 1.02 (9 H), 2.55, 2.67 (3 H), 3.52, 3.60 (2 H each), 3.85 (3 H, OCH_3)	6.62 (dd, J_o = 8.6, J_m = 2.5 Hz, 1 H, H5), 6.71 (s, 1 H, H3), 6.78 (d, 1 H, H3′), 7.30 (d, 1 H, H6′), 8.10 (s, 1 H, H6)
14a	1.11 (9 H, $C(CH_3)_3$), 2.20, 2.24, 2.26, 2.28, 2.38 (3 H each), 3.40 (2 H)	6.94 (s, 1 H, H6), 7.10−7.20 (m, 3 H, H3′,4′,6′)
14b	1.12 (9 H, $C(CH_3)_3$), 2.13, 2.23, 2.25, 2.42 (3 H each), 3.40 (2 H)	6.95 (s, 1 H, H6), 7.24 (d, J_o = 7.9 Hz, 2 H, H3′,5′), 7.70 (d, J_o = 8.2 Hz, 2 H, H2′,6′)
14c	1.12 (9 H), 2.14, 2.23, 2.25, 2.39 (3 H each), 3.40 (2 H)	6.95 (s, 1 H, H6), 7.25−7.40 (m, 2 H, H4′,5′), 7.55 (d, J_o = 7.3 Hz, 1 H, H6′), 7.64 (d, J_m = 0.5 Hz, 1 H, H2′)
14d	1.11 (9 H), 2.20, 2.23, 2.25, 2.46 (3 H each), 3.39 (2 H)	6.95 (s, 1 H, H6), 7.15−7.42 (m, 4 H, H3′,4′,5′,6′)

		Analysis (%) Calcd/Found						Analysis (%) Calcd/Found		
compd	molecular formula	C	H	N	Cl	compd	molecular formula	C	H	S
3a	$C_{18}H_{19}NO_3$	72.71	6.44	4.71		**10a**	$C_{12}H_{18}O$	80.85	10.18	
	(297.4)	72.54	6.41	4.60			(178.3)	81.13	10.20	
3b	$C_{18}H_{19}ClO$	75.38	6.68		12.36	**10b**	$C_{14}H_{22}O$	81.50	10.75	
	(286.8)	75.22	6.83		12.37		(206.3)	81.76	10.95	
3e	$C_{19}H_{22}O_2$	80.82	7.85			**11b**	$C_{16}H_{21}F_3O_5S$	50.26	5.54	8.38
	(282.4)	80.77	7.72				(382.4)	50.29	5.54	8.40
4a	$C_{16}H_{15}NO_4$	67.36	5.30	4.91		**12**	$C_{27}H_{36}O_5$	73.61	8.23	
	(285.3)	67.20	5.16	4.74			(440.6)	73.48	8.22	
5a	$C_{17}H_{17}NO_3$	72.07	6.05	4.94		**14a**	$C_{23}H_{30}O_2$	81.61	8.93	
	(283.3)	72.22	5.94	4.85			(338.5)	81.56	8.98	
5b	$C_{17}H_{17}ClO$	74.86	6.28		13.00	**14b**	$C_{22}H_{28}O_2$	81.44	8.70	
	(272.8)	74.64	6.23		12.86		(324.5)	81.45	8.80	
8a	$C_{18}H_{20}O_4$	71.98	6.71			**14c**	$C_{22}H_{28}O_2$	81.44	8.70	
	(300.4)	71.88	6.76				(324.5)	81.44	8.95	
8b	$C_{19}H_{22}O_5$	69.07	6.71			**14d**	$C_{22}H_{28}O_2$	81.44	8.70	
	(330.4)	68.98	6.81				(324.5)	81.33	8.42	

			Analysis (%) Calcd/Found		
compd		molecular formula	C	H	Cl
	Methyl Ester of Triflates				
1b	2.27 (s, 6 H, CH_3), 3.90 (s, 3 H, OCH_3), 7.08 (s, 2 H, H3,5)	$C_{10}H_{11}ClO_2$	60.46	5.58	17.85
		(198.7)	60.28	5.48	17.86
11a	1.04 (s, 9 H, $C(CH_3)_3$), 2.60 (s, 3 H, CH_3), 3.62 (s, 2 H, CH_2), 3.85 (s, 3 H, OCH_3), 6.70−6.75 (m, 2 H, H3,5), 7.90−7.95 (m, 1 H, H6)	$C_{14}H_{20}O_3$	71.16	8.53	
		(236.3)	71.01	8.64	
11b	1.10 (s, 9 H, $C(CH_3)_3$), 2.21, 2.25, 2.43 (each s, 3 H, CH_3), 3.35 (s, 2 H, CH_2), 3.86 (s, 3 H, OCH_3), 7.50 (s, 1 H, H6)	$C_{16}H_{24}O_3$	72.69	9.15	
		(264.4)	72.59	9.23	

[a] Chemical shift values (δ) observed in ppm relative to TMS as internal standard.

4-(2,2-Dimethylpropoxy)methylbenzoyl Trifluoromethanesulfonates 11. (a) Bromination to bromo(2,2-dimethylpropoxy)methylbenzenes was carried out according to ref 34; from **10a** (32.6 g, 0.183 mol) in acetic acid (120 mL) and bromine (28.9 g, 0.181 mol) in acetic acid (70 mL); yield after twice distillation: 34.2 g (73%) colorless oil, bp 132 °C/8 Torr. From **10b** (53.5 g, 0.26 mol) in acetic acid (300 mL), sodium acetate (21.3 g, 0.26 mol), and bromine (41 g, 0.26 mol) in acetic acid (70 mL); yield after recrystallization from MeOH (700 mL): 67.2 g (91%) colorless crystals, mp 43 °C.

(b) The Grignard reaction to the corresponding acids was carried out according to ref 35 with initiation of the reaction with 1,2-dibromoethane and ultrasound treatment; from Mg (3.5 g, 0.144 mol) in THF (150 mL), bromide of **10a** (34.2 g, 0.133 mol) in THF (100 mL), and CO_2 (300 g, 6.8 mol) in THF (400 mL); yield after

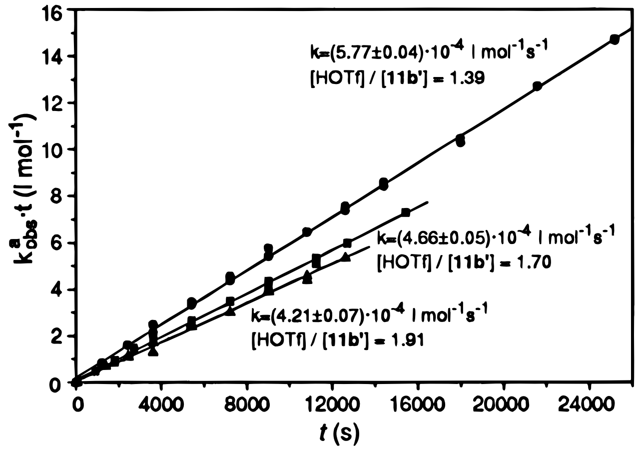

Figure 9. Second-order kinetics of acylations of **2e** with **11b′**.

recrystallization from chloroform/hexane: 21.3 g (72%) colorless crystals, mp 136 °C. From Mg (5.7 g, 0.235 mol) in THF (50 mL), bromide of **10b** (63.3 g, 0.222 mol) in THF (120 mL) and CO_2 (500 g, 11.4 mmol) in THF (500 mL); yield after recrystallization from chloroform/petroleum ether: 44.6 g (81%) colorless crystals, mp 186 °C.

(c) Chlorination of acids to acid chlorides was carried out by refluxing in thionyl chloride for 3 h and subsequent distillation; from acid of **10a** (10 g, 45 mmol) in 20 mL of thionyl chloride; yield: 10 g (91%) colorless solidifying oil, bp 88 °C/0.05 Torr. From acid of **10b** (6.5 g, 26 mmol) in 20 mL of thionyl chloride; yield: 6.5 g (93%) colorless solidifying oil, bp 104−106 °C/0.0005 Torr, mp 62.5 °C.

(d) **11a** was prepared as described below from 4-(2,2-dimethylpropoxy)methylbenzoyl chloride (0.893 g, 3.7 mmol) in 10 mL of DCE and $AgOSO_2CF_3$ (AgOTf)[23d] (0.952 g, 3.7 mmol) in 10 mL of DCE but decomposed after workup.

In case of **11b**, AgOTf (0.82 g, 3.2 mmol) was added at 0 °C portionwise to a stirred solution of 4-(2,2-dimethylpropoxy)-2,3,5-trimethylbenzoyl chloride (0.78 g, 2.9 mmol) in 1,1,2-trichlorotrifluoroethane (15 mL). After stirring at 0 °C for 1 h in the absence of light precipitated AgCl was filtered off, and the filtrate was concentrated by removal of the solvent *in vacuo*. Removal of solvent traces *in vacuo* at 0.001 Torr (6 h) yielded 1.10 g (99%) **11b** as brown oil. Data see Table 3.

Methyl 5-(4-(2,2-Dimethylpropoxy)-2-methylbenzoyl)-4-(2,2-dimethylpropoxy)-2-methylbenzoate (12). A solution of **11a** [prepared from AgOTf (0.952 g) and acid chloride (0.893 g)] was allowed to stand at room temperature for 2 h before mixing with 50 mL of methanol. After aqueous workup[23c] the mixture was chromatographed on silica gel with petroleum ether/ethyl acetate (15:1) to yield 0.05 g (6%) **12**.

Solutions of triflates were prepared at room temperature in DCE either by weighing (distillable compounds) or by adding a solution of the corresponding acid chloride in 10 mL DCE to a stirred suspension of AgOTf (1.1 equiv) in 10 mL of DCE. After 0.5 h precipitated AgCl was filtered off and washed with 2 mL of DCE. The combined filtrates were transferred to a 25 mL graduated flask under Ar atmosphere and filled up with DCE. The concentration was determined by GC from at least two samples.

For competitive conversions either 10 mL of a solution of one aromatic (0.04 M) in DCE was mixed at room temperature with 40 mL of a solution of two triflates (1:1, each ca. 0.025 M, exact ratio determined by GC) in DCE or 30 mL of a solution of two aromatics (each 0.33 M) in DCE were mixed with 20 mL of a solution of triflate (ca. 0.05 M) in DCE. The samples taken in the course of reaction were determined by GC.

Kinetic Measurements. To 22 mL of a solution of **11b** (c = 61.6−208.8 mM) in DCE containing HOTf or base **13** in a 25 mL graduated Schlenk flask, standing at 25 ± 0.2 °C for 1 h, the aromatic was added, the flask was filled up with DCE, and the reaction was started by shaking. Samples were taken via syringe at different times for derivatization and GC analysis and in the presence of **13** just after that additionally for IR measurements. The extinction at $\nu = 2188$ cm^{-1} was determined using spectra at the end of reaction (conversion >98%) as a reference. From the known extinction coefficient and the measured path length d[36] the concentration of **11b′** was calculated. In order to obtain second-order rate constants in presence of **13** velocities v were calculated from concentration-time data averaged before and after the specified time. The slope of the plot v versus the product of concentration of **11b′** and aromatic (calculated from concentration-time data) corresponds to k^{b}_{obs}. In presence of HOTf the second-order rate constants were determined from the integrated rate law given in the literature.[37]

IR Extinction Coefficient of 11b′. Aliquots of a stock solution of **11b** ($c = 0.172 \pm 5$ M) in DCE were mixed with the same volume of a solution of HOTf (0.402 M) in DCE. The mixtures were diluted to a known volume, and the IR spectra were recorded. The extinction was calculated from the difference to a solution of **13** and HOTf in DCE in order to rule out weak hydrogen bond absorptions between $\nu = 2200-2400$ cm^{-1}. The values reveal good linearity for concentrations up to 0.039 M ($R = 0.9996$, 6 points).

Gas Chromatography. Samples (0.5 or 1 mL) were mixed with methanol (1 mL) and if necessary with 1 mL of a solution of the internal standard 1,3-dinitrobenzene (competitive conversions) or **13** (kinetic studies in presence of HOTf). After 1 h the mixture was extracted with 1 mL of aqueous Na_2CO_3 solution (5%). The aqueous phase was extracted twice with DCE (1 mL), and the combined extracts were dried ($MgSO_4$), filtered, and used for GC analysis.

Absolute concentrations were calculated from the measured integrals of separated compounds using specific responce factors[38] for methyl esters and/or products relative to the used internal standards.

Preparation of Ketones 14b−d. At −15 °C **10b** (2.06 g, 10 mmol) was added dropwise to a stirred solution of 4-, 3-, or 2-methylbenzoyl chloride[39] (1.6 g, 10 mmol) and $FeCl_3$ (1.6 g, 10 mmol) in 10 mL of DCE. After stirring for a further 3 h at 0 °C the reaction mixture was hydrolyzed with 20 g of ice, stirred for 1 h, and extracted three times with dichloromethane (20 mL each). The combined extracts were washed with aqueous NaOH (5%) and water and dried ($MgSO_4$), and the solvent was removed *in vacuo*. **14b** and **14c** were recrystallized from *n*-hexane; yield of colorless crystals: 2.41 g (74%) **14b**, mp 97 °C; 2.20 g (68%) **14c**, mp 88 °C. **14d** was chromatographed on silica gel with petroleum ether/dichloromethane (1:1); yield: 2.1 g (65%) as colorless oil. Data see Table 3.

Acknowledgment. Dedicated to Professor Rolf Gleiter on the occasion of his 60th birthday. This work was supported by the Fonds der Chemischen Industrie.

JA9624331

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