Trifluoroacetic Acid-catalysed Transacylation of Arenes by Acylpentamethylbenzene

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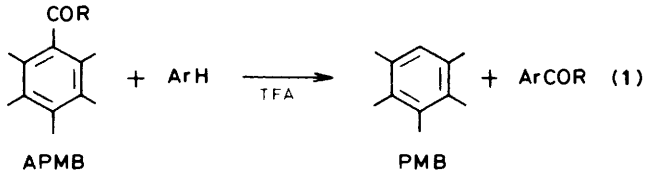
Facile transacylation between acylpentamethylbenzene and activated arenes such as anisole was found to occur in boiling trifluoroacetic acid (TFA). The mechanism for the transacylation between acetylpentamethylbenzene (AcPMB) and anisole with TFA was elucidated by means of product isolation and kinetics. The reaction proceeds *via* reversible protodeacetylation of AcPMB involving an *ipso*-protonated intermediate B to give pentamethylbenzene and acetic trifluoroacetic anhydride followed by irreversible acetylation of anisole by the mixed anhydride. The mechanism resulting in an *ipso*-protonated intermediate B was deduced from the reaction of acetylmesitylene with [^{2}H] TFA as well as from the rate of deacetylation of 3,5-dideuterioacetylmesitylene with TFA. The formation of such an intermediate was also independently confirmed by ^{13}C n.m.r. spectroscopic studies on AcPMB in superacid solutions under stable ion conditions.

The reversibility of Friedel–Crafts acylation is a topic of substantial interest.[1,2] Intra- and inter-molecular exchange of the acyl group of aromatic ketones have been extensively studied. Acid-catalysed transfer of an acyl group from one aromatic nucleus to another (transacylation) is believed to proceed *via* a Wheland intermediate resulting from the protonation of the acyl-group-bearing carbon atom (*ipso*-protonation). Baddeley and Pendleton have reported a transacetylation reaction of acetyldurene.[3] Treatment of acetyldurene with an excess of aluminium chloride at 100 °C gave diacetyldurene and polymethylbenzene, besides acetylprehnitine as the major product. Subsequently, Scholsberg and Woodbury have reinvestigated the possibility of transacetylation from tetramethylacetophenones to arenes in the presence of strong acids such as aluminium chloride, aluminium chloride–water, and hydrogen fluoride–antimony pentafluoride (5:1).[4] From this study they concluded that the acetophenones are predominantly *O*-protonated in the presence of strong acids, but that the transacetylation step requiring a second *ipso*-protonation of the *O*-protonated intermediate did not occur under the given reaction conditions. However, Gore *et al.*, in their continuing studies on transacylations, have found acetyl exchange in the reaction of acetylmesitylene with ^{14}C-labelled acetyl chloride under Friedel–Crafts reaction conditions.[5,6] More recently, Olah and co-workers have carried out deacetylation of a few hindered aromatic ketones, catalysed by the solid superacid Nafion-H.[7]

We previously reported the transacylation from 2-acyloxypyridines,[8] *N*-acylimidazoles,[9] or acylpolymethylbenzenes[10] to arenes in trifluoroacetic acid (TFA). In our continuing studies on the aromatic transacylations, we now wish to report detailed mechanistic studies on the transacylation between acylpentamethylbenzenes (APMB) and arenes, with TFA as the catalyst.

Results

Transacylation between APMBs and Arenes.—When a mixture of an acetylpentamethylbenzene (AcPMB) and an arene was heated in TFA under reflux, pentamethylbenzene (PMB) and the corresponding acetylarene were obtained. Such transacylation was also observed with other alkanoyl- and aroyl-pentamethylbenzenes. The results are summarized in Table 1. The yield of PMB increased with the electron-donating nature of the substituents on the aroyl ring.



The transacylation reactions between AcPMB and anisole with TFA were attempted in the presence of some additives. The addition of 1 equiv. of sodium trifluoroacetate with respect to AcPMB lowered yields of both PMB and acetylanisole (Table 1, entries 11 and 12), while the addition of silver or sodium triflates remarkably increased their yields (entries 14 and 16).

When a mixture of anisole and acetic trifluoroacetic anhydride, freshly prepared, was heated in TFA under reflux for 10 h, acetylanisole was obtained in 64% yield. The reaction of PMB with the mixed anhydride for 15 h afforded a mixture of PMB and AcPMB in a 38:62 ratio.

Kinetics of Protodeacylation of APMBs.—In order to gain insight into the transacylation mechanism, the reaction of AcPMB with anisole in refluxing TFA was studied in detail. Plots of typical product composition *versus* reaction time for the reaction in the presence of 2 equiv. of anisole are shown in Figure 1.

In the absence of anisole, the reaction attained an equilibrium after 2 h with 40% formation of PMB. In the presence of anisole, the amount of PMB and acetylanisole increased with reaction time. However, the rate of formation of PMB is different from that of acetylanisole; in particular an induction period was observed in the latter. The apparent rate constant for the formation of PMB was determined by the first-order kinetic plots of AcPMB under low conversion conditions. The results are summarized in Table 2. The rate constant obeys pseudo-first-order kinetics with respect to AcPMB in a solution with a large excess of TFA (more than 50-fold excess). It is clearly seen that the rate is independent of the concentration of anisole, even

Table 1. Results of the transacylation between APMB and arene with TFA

Entry	Acyl group in APMB	Arene	Reaction conditions: Molar ratio *vs.* APMB: Arene	Reaction conditions: Molar ratio *vs.* APMB: Additive	Reaction conditions: Time (h)	Product yield (%): Acylarene	Product yield (%): PMB
1	MeCO	Anisole	1		20	65 [a]	98
2	MeCO	Fluorene	1		10	44 [b]	99
3	MeCO	Thiophene	1		10	29 [c]	98
4	MeCO	*m*-Dimethoxybenzene	1		10	37 [d]	99
5	$MeCH_2CH_2CO$	Anisole	2		5	75 [a]	100
6	Me_2CHCO	Anisole	2		5	49 [a]	97
7	Me_3CCO	Anisole	2		5	43 [a]	96
8	PhCO	Anisole	2		5	18 [a]	40
9	*p*-MeC_6H_4CO	Anisole	2		5	27 [a]	48
10	*p*-ClC_6H_4CO	Anisole	2		5	2 [a]	20
11	MeCO	Anisole	2		0.5	13 [a]	33
12	MeCO	Anisole	2	CF_3CO_2Na 1	0.5	trace	26
13	MeCO	Anisole	2	CF_3CO_2Na 2	0.5	13 [a]	38
14	MeCO	Anisole	2	CF_3SO_3Na 1	0.5	24 [a]	77
15	MeCO	Anisole	2	CF_3SO_3Na 2	0.5	36 [a]	92
16	MeCO	Anisole	2	CF_3SO_3Ag 2	0.5	36 [a]	93

[a] A mixture of *p*- and *o*-acylanisole. [b] 2-Acetylfluorene. [c] 2-Acetylthiophene. [d] 2,4-Dimethoxyacetophenone.

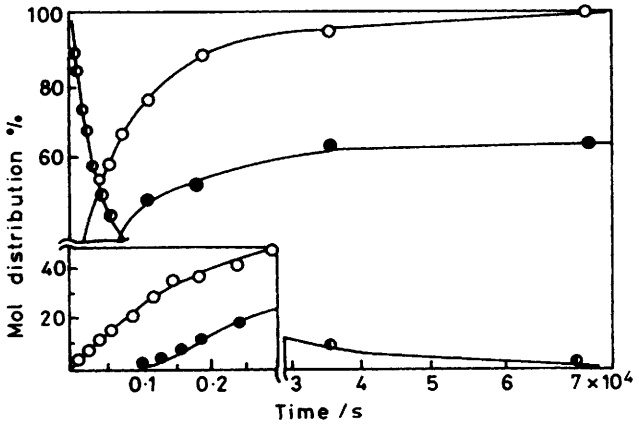


Figure 1. Change in reactant and product compositions in the reaction of AcPMB with anisole in TFA: ○ PMB, ◐ AcPMB, ● acetylanisole.

with a 20-fold excess. In contrast, the reaction was influenced by the addition of sodium trifluoroacetate or triflate. Figure 2 shows the plot of the rate constant *versus* the molar ratio of the added salt to AcPMB.

On the addition of sodium trifluoroacetate, the rate constant first decreased and then increased gradually with the increase in the molar ratio of the salt, while with sodium triflate the increase in rate was directly proportional to the amount of added salt. The initial rate depression seen in the case of the trifluoroacetate salt was not observed. In addition, the rate in [^{2}H]TFA solution decreased by a factor of 3.32 relative to that in TFA (Table 2, entry 7).

First-order rate constants for the protodeacylation of a variety of acylpolymethylbenzenes were determined in a similar manner. The results are collected in Table 3. The reaction was also promoted by the electron-donating methyl groups at the 2- and 6-position of the benzene ring. In diaryl ketone systems, the reaction was accelerated by electron-donating groups at the 4- or 4′-position of the rings. In aryl alkyl ketone systems, the protodeacylation rate depended on the nature of the alkyl group on the aliphatic acyl moiety. A t-butyl group slightly lowered the rate compared with a methyl group. The rate for

Table 2. First-order rate constants for the formation of PMB in the reaction of AcPMB with anisole in boiling TFA

Entry	Molar ratio of reagents *vs.* AcPMB [a]: TFA	Anisole	Salt	$10^4k/s^{-1}$	(r) [b]
1	100	2.0		2.05 ± 0.004	
2	50	2.0		2.06	(0.997)
3	100	0.5		2.02	(0.997)
4	100	1.0		2.01	(0.994)
5	100	1.2		2.02	(0.993)
6	100	20.0		2.10	(0.994)
7	100 [c]	2.0		0.62 ± 0.008	
8	100	2.0	CF_3CO_2Na 0.15	1.18 ± 0.03	
9	100	2.0	CF_3CO_2Na 0.40	1.33 ± 0.03	
10	100	2.0	CF_3CO_2Na 1.00	1.41 ± 0.05	
11	100	2.0	CF_3CO_2Na 1.50	1.67 ± 0.10	
12	100	2.0	CF_3CO_2Na 1.80	2.00	(0.985)
13	100	2.0	CF_3CO_2Na 2.00	2.34 ± 0.1	
14 [d]	100	2.0	CF_3SO_3Na 0.50	7.79	(0.984)
15 [d]	100	2.0	CF_3SO_3Na 1.00	8.51	(0.983)
16 [d]	100	2.0	CF_3SO_3Na 2.00	10.6	(0.988)

[a] $[AcPMB]_0$ = 0.131 M in TFA. [b] Correlation coefficient for the first-order rate plots. [c] [^{2}H]TFA was used as the acid. [d] The reaction was too fast to undertake the first-order plots under low conversion conditions.

deuterioacetylpentamethylbenzene was found to decrease by a factor of 1.13 compared with that of AcPMB (entry 1 in Table 2 and entry 12 in Table 3).

The Reaction of Acetylmesitylene with Anisole in TFA.— When a mixture of equimolar amounts of acetylmesitylene and anisole was heated in TFA solution under reflux for 20 h, mesitylene and acetylanisole were obtained in 44.5% and 16.1% yield, respectively. The rate constants for the deacetylation of acetylmesitylene and 1-acetyl-3,5-dideuteriomesitylene were determined (Table 3, entries 13 and 14). The rate ratio of unlabelled to labelled ketones was found to be 0.72. The ketones were heated in the presence of anisole in TFA or [^{2}H] TFA under reflux. The deuterium content in the unreacted ketones was examined by ^{1}H n.m.r. measurements. The results are shown in Table 4, together with the yields of mesitylene. It can be seen

Table 3. First-order rate constants for the protodeacylation of acylpolymethylbenzenes in boiling TFA[a]

Entry	Acyl group in the ketone	Substituents at the position of the ketone 2-	3-	4-	5-	6-	$10^5\ k/s^{-1}$	(r)
1	MeCO	Me	Me	OMe	Me	Me	5.57	(0.987)
2	MeCO	Me	Me	Me	H	Me	2.93	(0.999)
3	MeCO	Me	Me	H	Me	Me	0.245	(0.995)
4	MeCO	Me	Me	Me	Me	H	0.044	(0.993)
5	$MeCH_2CO$	Me	Me	Me	Me	Me	23.9	(0.994)
6	$MeCH_2CH_2CO$	Me	Me	Me	Me	Me	27.8	(0.992)
7	Me_2CHCO	Me	Me	Me	Me	Me	26.9	(0.993)
8	Me_3CCO	Me	Me	Me	Me	Me	19.2	(0.992)
9	PhCO	Me	Me	Me	Me	Me	5.54	(0.992)
10	p-MeC_6H_4CO	Me	Me	Me	Me	Me	6.31	(0.995)
11	p-ClC_6H_4CO	Me	Me	Me	Me	Me	1.73	(0.999)
12	CD_3CO	Me	Me	Me	Me	Me	18.2 ± 0.06	
13	MeCO	Me	H	Me	H	Me	0.66 ± 0.01	
14	MeCO	Me	D	Me	D	Me	0.92 ± 0.07	

[a] $[Acylpolymethylbenzene]_0$ = 0.131M; $[Anisole]_0$ = 0.262M in TFA.

Table 4. The results of proton–deuteron exchange reactions of acetylmesitylene and 1-acetyl-3,5-dideuteriomesitylene

Entry	Ketone	Acid	Reaction time (h)	Deuterium-substitution degree of 3,5-ArH (%)	Yield of mesitylene (%)
1	Acetylmesitylene	[^{2}H]TFA	2	18	4.7
2	Acetylmesitylene	[^{2}H]TFA	16	64	21
3	1-Acetyl-3,5-di-deuteriomesitylene	TFA	2	78	8.3
4	1-Acetyl-3,5-di-deuteriomesitylene	TFA	4	63	14

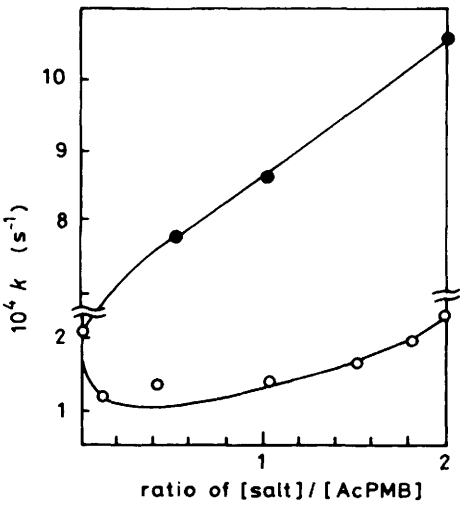
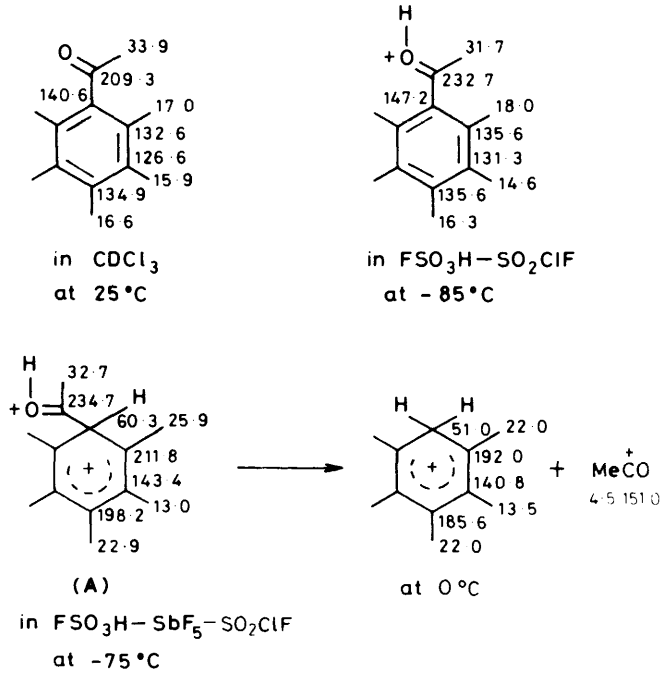


Figure 2. Plots of k *versus* molar ratios of the added salt to AcPMB: ○ CF_3COONa, ● CF_3SO_3Na.



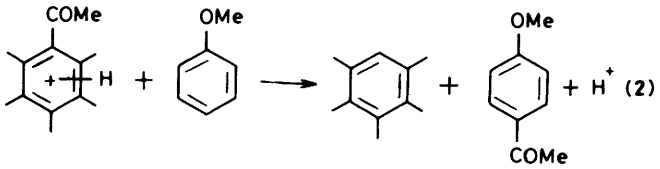
Scheme.

that proton–deuteron exchange at the 3- and 5-position of the ketones occurs prior to the deacetylation.

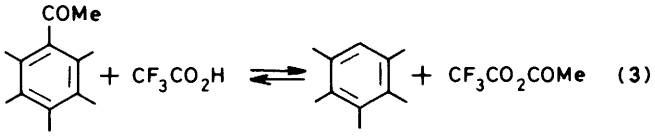
^{13}C N.m.r. Measurements of AcPMB in Superacids.—^{13}C N.m.r. spectra of AcPMB were measured under long lived stable ion conditions. The chemical shifts were assigned for each species by comparing the data for polymethylbenzenium ions previously reported by Olah,[11] and are shown in the Scheme. In FSO_3H–SO_2ClF solution at −85 °C, AcPMB was clearly *O*-protonated at the acetyl group. However, on addition of AcPMB to much stronger FSO_3H–SbF_5–SO_2ClF solution, the chemical shifts for the ring carbons changed considerably, indicating deshielded sp^2 and sp^3 carbons. This suggests the formation of the *C*-protonated benzenium onium ion (**A**). When the temperature of the solution was raised to 0 °C, irreversible deacetylation occurred to give protonated pentamethylbenzenium ion and acetylium ion.[12]

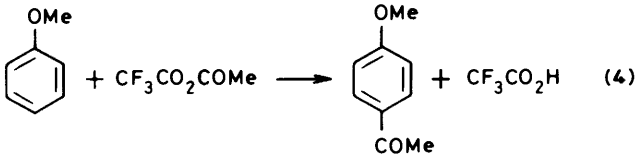
Discussion

Transacylation between APMB and Arene.—The results shown in Table 1 indicate that intermolecular acyl group transfer from APMB to arene occurs. It was found that yields of acylarenes resulting from the transacylation were always lower than those of PMB. In the reaction of anisole with AcPMB in TFA, the rate for the formation of PMB is found to be independent of the concentration of anisole. Accordingly, the transacetylation catalysed by TFA does not seem to proceed directly from the protonated AcPMB to anisole [as in equation (2)].

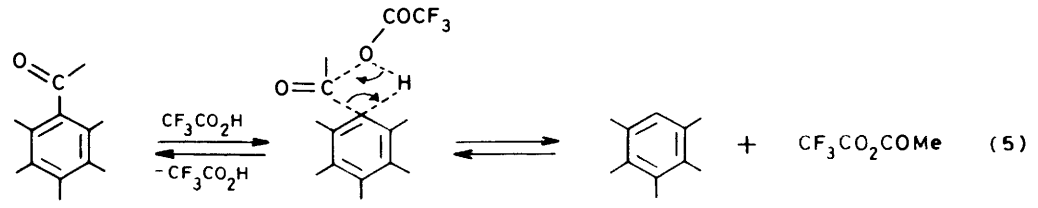


AcPMB in boiling TFA without anisole affords a reversible mixture of PMB and AcPMB, in which the ratio of both compounds is in excellent agreement with that obtained in the reaction of PMB with acetic trifluoroacetic anhydride in boiling TFA. Consequently, the transacetylation from AcPMB to anisole in TFA seems to proceed in two steps consisting of a reversible protodeacetylation of AcPMB to give PMB and acetic trifluoroacetic anhydride, and a subsequent reacylation of arene with the resulting mixed anhydride, as shown in equations (3) and (4).

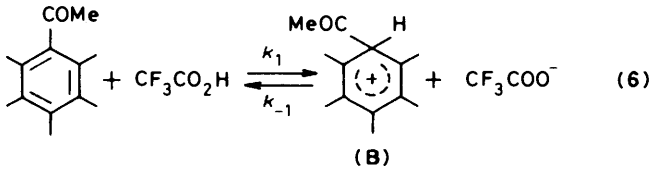


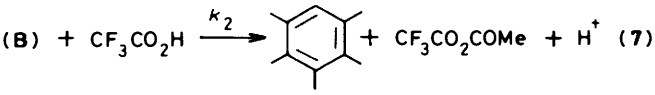


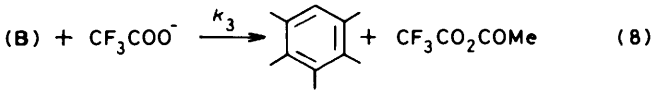
Protodeacylation Mechanism of APMB by TFA.—Protodeacylation of acetylmesitylene and 2,6-dimethylacetophenone with strong sulphuric acid was studied by Schubert and Latourette in detail.[13] The reaction was found to proceed *via* a mechanism involving a first-order decomposition of the conjugate acid of the ketones. We have examined the protodeacylation reaction of APMB in TFA with respect to substituent effects, isotope effects of the acid or the leaving group, and added salt effects. The substituent effects and the high solvent isotope effect observed on the deacylation of acylpolymethylbenzenes indicate that the reaction involves an electrophilic protonation process in the rate-determining step. The rate difference between deuterioacetyl and acetylpentamethylbenzene seems to be due to a primary kinetic isotope effect for the elimination of the acetyl group.* Therefore, these results might suggest a synchronous process involving electrophilic protonation and nucleophilic abstraction of acetyl group with TFA as in equation (5)



However, the above mechanism (5) can be clearly ruled out because of the observed salt effects which significantly alter the rate of deacylation. The following three reactions (6), (7), and (8) were then considered.







Applying the steady-state approximation for the intermediate (**B**), the rate of formation of PMB can be expressed by the following equation (9). The assumption that $k_{-1} \gg k_3$ and

$$\frac{d[PMB]}{dt} = \frac{k_1[AcPMB][TFA]\{k_2[TFA] + k_3[CF_3COO^-]\}}{k_2[TFA] + (k_{-1} + k_3)[CF_3COO^-]} \quad (9)$$

$k_2[TFA] \gg k_3[CF_3COO^-]$ leads to following rate equation (10).

$$\frac{d[PMB]}{dt} = \frac{k_1k_2[AcPMB][TFA]^2}{k_2[TFA] + k_{-1}[CF_3COO^-]} \quad (10)$$

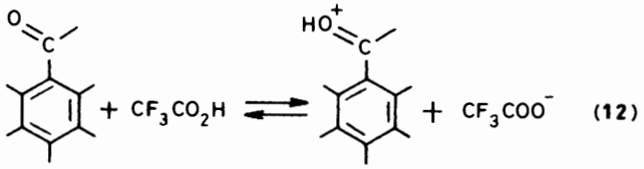
This is a general equation similar to those observed in aliphatic nucleophilic substitution reactions.[15] The rate obeys the first-order kinetics in AcPMB under large excess of TFA in the initial low-conversion regions.

$$\frac{d[PMB]}{dt} = k[AcPMB] \quad (11)$$

* If this is due to the β-deuterium secondary isotope effect for the addition of trifluoroacetic acid to the carbonyl group, then the k_H/k_D should be less than unity since the effect is considered to arise from changes in the β-CH (CD) force constants induced by variation in hyperconjugation of the electron of β-CH (CD) bonds into the carbonyl group.[14]

The TFA molecule seems to play two major roles: one as an acid, protonating AcPMB in reaction (6) and the second as a nucleophile, abstracting the acetyl group in reaction (7). If reaction (7) contributes to the rate-determining step in a similar way to reaction (6), then the difference in the leaving group ability of the acyl group would appear in the apparent rate constant. Indeed, this was shown by the experimental results. A slight decrease in the rate of elimination of a trimethylacetyl compared to an acetyl group can be ascribed to the steric hindrance of the former to the approach of TFA towards the carbonyl carbon of the intermediate (**B**). The observed high acid isotope effect also might arise in part from the contribution of reaction (7).

One can also consider a pre-fast equilibrium reaction of AcPMB in TFA, *i.e.* the protonation–deprotonation reaction (12). However, the direct transformation of the *O*-protonated intermediate to the *C*-protonated intermediate (**B**) may not be feasible because of an unfavourable transition state [even *via* proton transfer to the 3- or 5-position (*vide infra*)]. Hence, reaction (12) is irrelevant to the kinetic treatment.



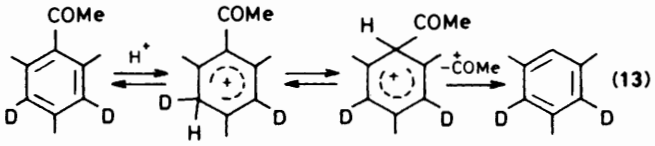
(12)

The addition of small amounts of sodium trifluoroacetate to the reaction system lowers the rate in a way similar to the common ion effects observed in S_N1 reactions.[16] The common salt effect observed here suggests that the structure of the intermediate is of a free or loose ion-pair nature. Hence, a concentration of the counteranion of electrophiles can give important information about the nature of the transition state of aromatic electrophilic substitutions. To the best of our knowledge, such effects have never been explored, and thus the common salt effects observed here appear to be the first such example in aromatic electrophilic substitutions. Such a situation is possible here because the intermediate (**B**) is well stabilized by five methyl groups, and the TFA medium is quite non-nucleophilic.

When a large amount of trifluoroacetate salt is added to the system, the contribution of reaction (8) to the deacetylation would be more significant than that of reaction (7). Under these conditions, the added trifluoroacetate works against the common salt effect in equation (9). However, the degree of rate increase is not very much due to the fact that the rate depression by the common salt effect compensates for the rate increase. On the other hand, the addition of sodium triflate, which has no influence upon the equilibrium in equation (6), markedly increases the rate. This kinetic interpretation is consistent with the results of the transacylation of AcPMB with anisole (Table 1).

The existence of the *ipso*-protonated intermediate (at the acetyl group) has been confirmed by ^{13}C n.m.r. measurements of AcPMB under stable ion conditions. As Schlosberg and Woodbury reported,[3] protonation of the carbonyl oxygen of the acetyl group precedes ring carbon protonation, as indicated by the ^{13}C n.m.r. spectrum of AcPMB in FSO_3H. In much stronger magic acid, further protonation of the *ipso* ring carbon takes place (acetyl group attached) to provide the carbodication (**A**). The carbodication (**A**) was found to decompose irreversibly to acetylium cation and protonated pentamethylbenzenium ion at elevated temperatures.

The next important question was, what is the exact initial site of protonation of AcPMB in TFA? Direct *ipso*-protonation of the acetyl-group-bearing carbon seems unlikely, owing to the deactivation of that site by the electronegative carbonyl group. In deacetylations of acetylmesitylene with [^2H]TFA or 1-acetyl-3,5-dideuteriomesitylene with TFA, it has been found that proton–deuterium exchange at the 3- and 5-position of the aromatic ring occurs prior to deacetylation. Furthermore, the presence of deuterium atoms at the 3- and 5-position of acetylmesitylene was found to affect the rate of deacetylation.* These show that initial protonation of acetylmesitylene is at either the 3- or 5-position (the highest electron-density sites). Subsequent proton shifts seem to generate the *ipso*-protonated Wheland intermediate (the most stable benzenium ion). This mechanism is depicted in equation (13).



(13)

Based on the above observations, protonation of APMB with TFA should also proceed in a similar way. Consequently, the reaction mechanism for the transacylation from APMB to arene in boiling TFA appears to proceed first *via* ring protonation of the 3- or 5-position of APMB followed by a proton shift to provide the intermediate (**B**), which then deacetylates to give PMB and acyl trifluoroacetate (mixed anhydride). The mixed anhydride readily acylates the arene present in the same TFA solution.

Experimental

^1H N.m.r. spectra were recorded in deuteriochloroform with reference to internal tetramethylsilane on a JEOL-GX 270 Model spectrometer. ^{13}C N.m.r. spectra were recorded on a Varian Associates Model FT-80 n.m.r. spectrometer equipped with a low-temperature broad-band probe. The chemical shifts were measured from external (capillary) tetramethylsilane. Mass spectra were recorded on a JEOL-01SG2 Model spectrometer. The g.l.c. analyses were carried out on a Hitachi GC 163 Model gas chromatograph equipped with a hydrogen flame ionization detector and a stainless steel column (length 3 m, i.d. 3 mm) packed with 3% Dexil 300 GC on Chromosorb W. Product yields were calculated from the relative peak areas with respect to the internal standard (dibenzofuran) on a Takeda TR 2220A Model integrator after calibration for each authentic compound.

Materials.—Acylpolymethylbenzenes were prepared from polymethylbenzenes and acyl chloride following the usual Friedel–Crafts reaction procedure. Sodium trifluoroacetate was prepared by the reaction of trifluoroacetic acid with sodium hydride in dichloromethane at 0 °C and was thoroughly dried under vacuum at 110 °C prior to use. Acetic trifluoroacetic anhydride was prepared according to a literature procedure.[17]

Trideuterioacetylpentamethylbenzene. Pentamethylbenzene (18.2 g, 0.122 mol) was allowed to react with trideuterioacetyl chloride (12.0 g, 0.145 mol) in the presence of aluminium chloride (19.3 g, 0.145 mol) in dichloromethane (110 ml) to give the title compound (8.7 g, 36.5%), m.p. 83—84 °C (from methanol); δ($CDCl_3$) 2.15 (s, 6 H), 2.10 (s, 3 H), and 2.03 (s, 6 H)

* This seems to be the secondary kinetic isotope effect due to the pre-equilibrium of protonation–deprotonation at the 3- and 5-position of acetylmesitylene. The isotope effect on the change of hybridization from the sp^2 CH to the sp^3 CH can be roughly calculated as 0.75 at the reflux temperature (77 °C) of TFA. Ref. 15, p. 110.

(Found: C, 80.5; H + D, 10.7%; $M^{+\bullet}$, 193). Calc. for $C_{13}H_{15}D_3O$: C, 80.8; H + D, 10.9%; $M^{+\bullet}$, 193).

1-Acetyl-3,5-dideuteriomesitylene. Mesitylene (5.00 g, 41.6 mmol) was heated in a solution of [^{2}H]TFA (33.5 g, 291 mmol) and deuterium oxide (2.5 g, 12.5 mmol) at 60 °C for three days. The reaction mixture was then poured into ice–water and extracted with ether. After evaporation of the solvent, the deuterium content of the resulting residue was determined by ^{1}H n.m.r. analysis. This procedure was repeated until *ca.* 95% of protons of the aromatic ring were replaced by deuterium atoms. The resulting deuteriomesitylene was distilled under reduced pressure to obtain 1,3,5-trideuteriomesitylene (4.35 g, 85%). The thus prepared mesitylene (8.54 g, 69.3 mmol) was treated with acetyl chloride (6.53 g, 83.2 mmol) in the presence of aluminium chloride (11.1 g, 83.2 mmol) in dichloromethane (60 ml) at 0 °C. The crude product obtained by the usual work-up was distilled under reduced pressure to obtain the title compounds (8.1 g, 71%), b.p. 124 °C at 23 mmHg; δ($CDCl_3$) 6.83 (s, trace), 2.45 (s, 3 H), 2.27 (s, 3 H), and 2.22 (s, 6 H); the degree of deuterium substitution on the aromatic ring was 93% (by ^{1}H n.m.r.).

General Procedure for the Transacylation.—The typical procedure described is for the reaction of AcPMB with anisole. To a mixture of AcPMB (0.100 g, 0.526 mmol) and anisole (0.057 g, 0.526 mmol) placed in a 10 ml flask, was added trifluoroacetic acid (6.00 g, 52.6 mmol) and the mixture was heated under reflux for a given period, after which the reaction was quenched by the addition of an excess of cold 5% aqueous sodium carbonate, and the resulting oily product was extracted with ether (50 ml) containing dibenzofuran (0.100 g) (as the internal standard for g.l.c. analyses). The organic layer was washed with water and dried over anhydrous sodium sulphate. After evaporation of the solvent, the residue was dissolved in benzene and then analysed by g.l.c.

Kinetic Studies.—The typical procedure described is for the deacetylation of AcPMB. AcPMB (0.125 g, 0.657 mmol) and anisole (0.142 g, 1.31 mmol) were dissolved in TFA (5 ml) in a 10 ml flask. The mixture was immediately brought to reflux by immersing the reaction flask in an oil-bath maintained at 110 °C. After refluxing for a given period, the reaction mixture was worked in a similar manner as described earlier and analysed by g.l.c.

Proton–Deuteron Exchange Reaction of Acetylmesitylene.—A solution of acetylmesitylene (0.100 g, 0.616 mmol) and anisole (0.133 g, 1.23 mmol) in [^{2}H]TFA (5 ml) was heated under reflux for a given period. The mixture was worked up as above and analysed by g.l.c. and ^{1}H n.m.r. The degree of deuterium substitution in the unreacted acetylmesitylene was determined by ^{1}H n.m.r. by comparing signals of the ring protons (6.83 p.p.m.) with the 4-methyl protons (2.27 p.p.m.) as well as the acetyl protons (2.45 p.p.m.).

Preparation of Protonated Acetylpentamethylbenzenium Ion.—Well pulverized AcPMB (0.100 g) was suspended in sulphuryl chloride fluoride (2 ml) at −78 °C. To the suspension, a cold solution of fluorosulphuric acid–antimony pentafluoride (1:1) (2 ml) dissolved in sulphuryl chloride fluoride (2 ml) was added dropwise with vigorous stirring at −78 °C. A portion of the red coloured solution was taken out into a n.m.r. tube and was subjected to ^{13}C n.m.r. analysis. *O*-Protonated AcPMB was similarly prepared using fluorosulphuric acid in sulphuryl chloride fluoride.

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