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The Triflic Acid-Catalysed Deacylation and Decarboxylation of Polymethylbenzenecarbonyl Derivatives under Mild Conditions

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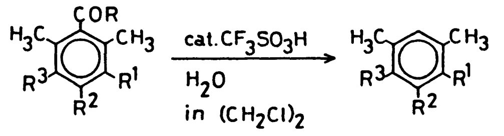
Synopsis. Sterically hindered acylarenes are deacylated to arenes in good yields on heating in boiling 1,2-dichloroethane containing a catalytic amount of triflic acid and water. Hindered arenecarboxylic acids undergo decarboxylation under the same conditions to give arenes in high yields.

It is known that sterically hindered aromatic ketones and carboxylic acids can undergo protodeacylation or decarboxylation in the presence of concd sulfuric acid,[1)] polyphosphoric acid,[2)] or Friedel-Crafts catalysts.[3)] However, the reaction of acylpolymethylbenzenes with these catalysts is accompanied by some side reactions, such as the sulfonation,[4,5)] disproportionation,[6)] or isomerization of alkyl groups in the substrates or products.[7,8)] Olah and his co-workers reported that perfluororesin sulfonic acid, "Nafion-H," is an efficient catalyst for the deacylation of hindered aromatic ketones in hot toluene or anisole.[9)] However, this procedure involves the problem of isolating the products from excess toluene or anisole. In addition, polymerized products result from the ketene formed during the deacetylation. We have previously reported on the transacylation between acylpolymethylbenzenes and some arenes in boiling trifluoroacetic acid (TFA).[10)] In that paper, we described how the presence of a nucleophile in TFA accelerates the protodeacetylation rate of acetylpentamethylbenzene (AcPMB).

We wish to report now that the addition of a small amount of water to TFA increases the protodeacetylation rate of AcPMB and that, therefore, the deacylation of a variety of acylarenes to arenes can be selectively performed with a catalytic amount of triflic acid (TFSA) in boiling 1,2-dichloroethane (DCE) containing a small amount of water. The decarboxylation of arenecarboxylic acids with this system will be described.



Scheme 1.

Results and Discussion

When AcPMB is heated in TFA under reflux, deacetylation proceeds to afford pentamethylbenzene (PMB). The apparent rate constant for the formation of PMB was determined in the presence of water. The rate

Table 1. First-Order Rate Constants for the Protodeacetylation of Acetylpentamethylbenzene (AcPMB) in Boiling TFA[a)]

Run	Molar ratio	Rate constant	r[b)]
	H_2O/AcPMB	$10^4k/s^{-1}$	
1[c)]	0	2.05±0.004	
2	0.2	3.22	0.999
3	0.5	3.74	0.997
4	1	4.08	0.998
5	2	4.50	0.996
6	3	4.18	0.998

a) $[AcPMB]_0$=0.131 M in TFA. b) Correlation coefficient for the first-order rate plots (8 points). c) Quoted from Ref. 10.

Table 2. Protodeacetylation of Acetylpentamethylbenzene (AcPMB) to Pentamethylbenzene (PMB)[a)]

Run	Acid	Molar ratio vs. AcPMB		Solvent	React. time	Yield of PMB	Recovery of AcPMB[b)]
		Acid	H_2O		h	%	%
1	TFA[c)]	100	—	—	2	40	60
2	TFA	100	0.3	—	1	71	30
3	TFA	100	0.6	—	1	75	27
4	TFA	100	1	—	1	76	20
5	TFA	100	5	—	1	99	1
6	TFA	100	11	—	1	97	1
7	TFA	5	2	DCE[d)]	5	8	92
8	TFA	2	1	DCE	5	0	99
9	TFSA[e)]	2	2	DCE	5	100	0
10	TFSA	0.5	2	DCE	5	100	0
11	TFSA	0.2	1	DCE	5	98	1
12	TFSA	0.5	—	DCE	5	56	17
13	TFSA	1.0	—	DCE	5	51	13

a) Carried out in boiling TFA or DCE. b) Determined by GLC. c) Trifluoroacetic acid. d) 1,2-Dichloroethane. e) Triflic acid.

constant obeys pseudo-first-order kinetics with respect to AcPMB in a solution with a large excess of TFA (more than a 50-fold excess) (Table 1). The results indicate that the addition of water into TFA promotes the deacetylation rate. The rate constant increased with the increase in the molar ratio of the added water. The effect of water was also confirmed in a preparative experiment. It can be seen from the results shown in Table 2 that the yield of PMB increases with the increase in the amount of water added. We found that TFA with a water content of ca. 15% works efficiently in the deacetylation of AcPMB. In order to save some of the TFA, the deacetylation was attempted in a DCE solution containing a small amount of water. The reaction with two equivalents of TFA in DCE did not occur at all, and the yield of PMB was only 8%, even with five equivalents of TFA. In contrast, the reaction using TFSA as an acid proceeded smoothly to give PMB in a quantitative yield. The deacetylation product can be obtained in a good yield even with a catalytic amount of TFSA. In the absence of water, though, the reaction was accompanied by some side reactions to result in a low yield of PMB and a low recovery of AcPMB.

A variety of pentamethylbenzenecarbonyl derivatives were subjected to deacylation or decarboxylation with TFSA in a DCE solution. The results are summarized in Table 3. Pentamethylbenzenecarbonyl derivatives, having not only alkanoyl but aroyl moieties, were deacylated to give PMB in satisfactory yields. The decarboxylation of pentamethylbenzoic acid was also efficiently performed under these conditions. However, in the case of ethyl pentamethylbenzoate, the yield of PMB was low and the starting ester was recovered.

Furthermore, various polymethylbenzenecarbonyl derivatives were reacted with catalytic amounts of TFSA in boiling DCE (Table 4).

As can be seen from the results listed in Table 4, the method works satisfactorily for sterically hindered alkyl aryl ketones, benzophenones, and benzoic acids, which have methyl groups at both the 2- and 6-positions. No side reactions have been observed.

Table 3. Protodeacylation and Decarboxylation of Pentamethylbenzenecarbonyl Derivatives (PMBC) with TFSA[a)]

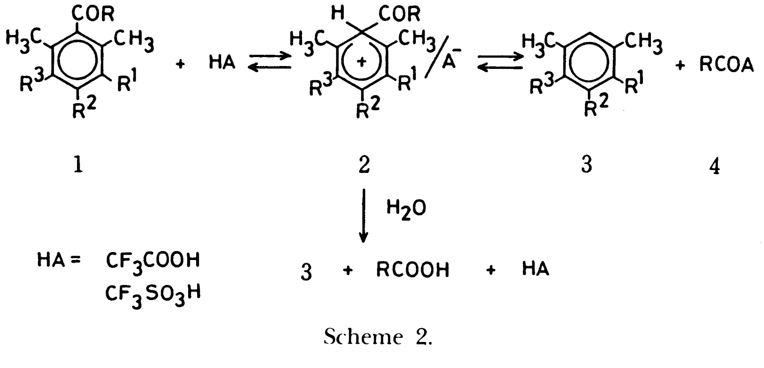
Run	Carbonyl group of PMBC	React. time h	Yield of PMB[b)] %
1	CH_3CO-	5	98
2	CH_3CH_2CO-	5	99
3	$CH_3CH_2CH_2CO$-	5	97
4	$(CH_3)_3CCO$-	5	99
5	$C_6H_5CH{=}CHCO$-	15	100
6	HOCO-	15	94
7	CH_3CH_2OCO-	15	18
8	p-$CH_3C_6H_4CO$-	5	91
9	p-ClC_6H_4CO-	15	90
10	p-FC_6H_4CO-	24	80
11	p-$CH_3OC_6H_4CO$-	24	93

a) Carried out with 0.5—2.0 equivalents of TFSA in boiling 1,2-dichloroethane containing ca. one equivalent of water. b) Determined by GLC.

Table 4. Protodeacylation and Decarboxylation of Polymethylbenzenecarbonyl Derivatives (POBC) with TFSA[a)]

Run	Carbonyl group of POBC	Substituent of the benzene ring 2-	3-	4-	5-	6-position	React. time h	Yield of methylbenzenes[b)] %
1	CH_3CO-	CH_3	CH_3	H	CH_3	CH_3	5	95
2	CH_3CO-	CH_3	H	CH_3	CH_3	CH_3	5	100
3	CH_3CO-	CH_3	H	CH_3	H	CH_3	5	98
4	CH_3CO-	H	CH_3	CH_3	CH_3	CH_3	5	4
5	HOCO-	CH_3	CH_3	H	CH_3	CH_3	5	80
6	HOCO-	CH_3	H	CH_3	CH_3	CH_3	5	100
7	HOCO-	CH_3	H	CH_3	H	CH_3	10	100
8	HOCO-	H	CH_3	CH_3	CH_3	CH_3	5	0
9	C_6H_5CO-	CH_3	CH_3	H	CH_3	CH_3	24	90

a) Carried out with 0.5 equivalent of TFSA in boiling 1,2-dichloroethane containing ca. one equivalent of water. b) Determined by GLC.



Scheme 2.

As regards the mechanism of the deacylation reaction, an ipso-protonated intermediate (**2**) at the ring C-atom attached to the acyl group may be assumed as has been reported before (Scheme 2).[10] In the absence of water, a conjugate base of the acids works as a nucleophile for the removal of the acyl group to give the hydrocarbon (**3**) and the mixed anhydride (**4**). The latter is known to acylate arenes in a TFA solution.[11,12] Thus in the deacetylation of AcPMB in boiling TFA, an equilibrium is reached with the formation of 40% of PMB.[10] When water is present in the solution, it works as a nucleophile to remove the acetyl group, thus giving PMB, TFA, and acetic acid. In the case of a stronger acid TFSA relative to TFA, the TFSA regenerated from a reaction of the intermediate **2** with water will work again for the ipso-protonation so that it may be enough in catalytic amount. Ethyl pentamethylbenzoate might be protonated at the alkoxyl oxygen to resist ipso-protonation to the ring carbon for the deethoxycarbonylation.

Experimental

Materials and Measurements: The acylpolymethylbenzenes were prepared from polymethylbenzenes and acyl chloride following the usual Friedel-Crafts reaction procedure. Commercial TFA (Peptide Institute) was used after distilling in the presence of a small amount of trifluoroacetic anhydride. The TFSA used was a commercial one (Aldrich). The GLC 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. The product yields were calculated from the relative peak area with respect to the internal standard (dibenzofuran) on a System Instruments Chromatocorder 11 after calibration for each authentic compound.

Kinetic Studies: AcPMB (0.125 g, 0.657 mmol) was dissolved in TFA (5 ml) containing a given amount of water 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 quenched by pouring it into an excess of a cold 5% aqueous sodium carbonate solution; the resulting oily product was extracted with ether containing dibenzofuran (0.100 g) (as the internal standard for GLC analysis). The organic layer was washed with water and dried over anhydrous sodium sulfate. After the evaporation of the solvent, the residue was dissolved in benzene and then analyzed by means of GLC.

General Procedure for the Deacylation: The typical procedure described is for the reaction of AcPMB with TFSA: To a solution of AcPMB (0.114 g, 0.600 mmol) in 1,2-dichloroethane (3 ml) containing water (20 μl, 1.2 mmol) placed in a 30 ml flask, was added TFSA (0.045 g, 0.300 mmol) in DCE (2 ml) and the mixture was heated under reflux for 5 h. After that, the reaction mixture was poured into an excess of a cold 5% aqueous sodium carbonate solution and then extracted with ether (50 ml) containing dibenzofuran (0.100 g). The organic layer was washed with water and dried over anhydrous sodium sulfate. After the subsequent evaporation of the solvent under reduced pressure, the residue was analyzed by means of GLC.

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