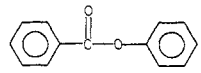
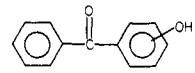
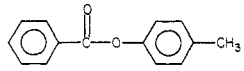
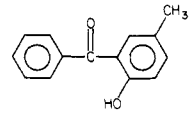
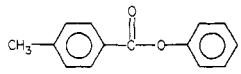
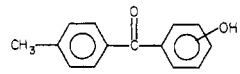
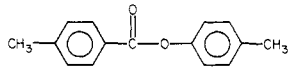
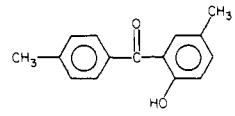
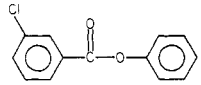
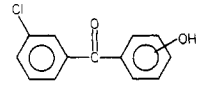
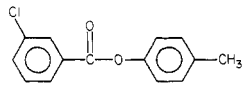
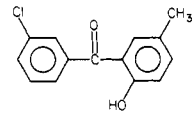
Table I. Fries Rearrangement over Nafion-H Catalyst

precursor	product(s)[a]	yield, %	ortho/para isomer ratio
		73	1:2
		70	
		63	2:5
		72	
		75	1:2.6
		71	

[a] The identity of all the products was established by ^1H and ^{13}C NMR spectroscopy.

General Procedure for Nafion-H-Catalyzed Fries Reaction. Into a solution of 10 mmol of the phenol ester in 50 mL of dry nitrobenzene[11] was added 100 mg of Nafion-H (prepared from Du Pont's commercial Nafion-501 resin K salt with nitric acid as described previously[1]) and mixture refluxed with stirring for 12 h. At the end of this period the solution was cooled, and the catalyst was filtered and washed with ether. The filterate was extracted with 10% NaOH (3 × 50 mL), and the basic aqueous solution was neutralized with 10% HCl. The product was extracted into ether and the ether layer washed well with saturated NaCl solution. Evaporation of the ether after drying over anhydrous sodium sulfate gave the hydroxyphenyl ketones. As the product hydroxyphenyl ketones consists of mixture of isomers they were conveniently analyzed by ^1H and ^{13}C NMR spectroscopy. The isomer distribution was determined by integration of characteristic ^1H NMR or NOE-suppressed ^{13}C NMR peaks of the product mixture.

Regeneration of Nafion-H Catalyst. After filtration the catalyst was washed with acetone and deionized water and dried overnight at 105 °C. Repeating the reaction with the regenerated catalyst gave results identical with one that used freshly activated catalyst.

Acknowledgment. Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

Registry No. Phenyl benzoate, 93-99-2; *p*-toluene benzoate, 614-34-6; phenyl *p*-toluate, 1900-85-2; *p*-toluene *p*-toluate, 15024-08-5; phenyl *m*-chlorobenzoate, 41998-17-8; *p*-toluene *m*-chlorobenzoate, 6280-49-5; *o*-hydroxybenzophenone, 117-99-7; *p*-hydroxybenzophenone, 1137-42-4; 2-hydroxy-5-methylbenzophenone, 1470-57-1; 2-hydroxy-4′-methylbenzophenone, 19434-30-1; 4-hydroxy-4′-methylbenzophenone, 134-92-9; 2-hydroxy-4′,5-dimethylbenzophenone, 26880-95-5; 3-chloro-2′-hydroxybenzophenone, 72090-60-9; 3-chloro-4′-hydroxybenzophenone, 61002-52-6; 3′-chloro-2-hyroxy-5-methylbenzophenone, 6280-54-2; Nafion-H, 63937-00-8.

(11) The reaction must be carried out under anhydrous conditions, otherwise acid catalyzed hydrolysis of the ester will be a competing reaction.

Catalysis by Solid Superacids. 18.[1] Nafion-H Perfluorinated Resin Sulfonic Acid Promoted Deacetylation and Decarboxylation of Aromatics

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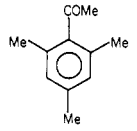
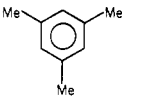
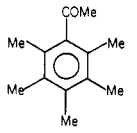
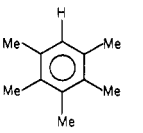
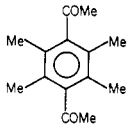
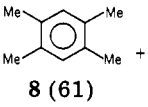
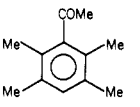
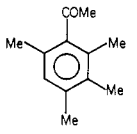
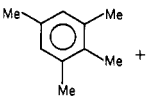
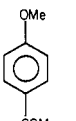
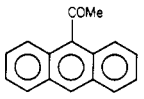
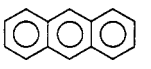
Transacetylation of aromatic ketones and the notion of reversibility of acetylation reactions under Friedel–Crafts conditions is a subject of continuing interest.

Baddeley first observed that acetyldurene reacted with $AlCl_3$ at 100 °C to give durene and diacetyldurene.[2] Deacetylation of 2,6-dimethylacetophenone and acetylmesitylene in protic acids was shown to be a first-order decomposition of the conjugate acid of the ketone.[3] Agranat et al. recently reported the rearrangement of 1-benzoylnaphthalene to 2-benzoylnaphthalene by heating with polyphosphoric acid (PPA).[4] Similarly, para ⇌ ortho acyl rearrangement occurred in PPA for fluorofluorenone at high temperatures.[5]

(1) For part 17 see: Olah, G. A.; Arvanaghi, M.; Krishnamurthy, V. V. *J. Org. Chem.*, previous note in this issue.
(2) Baddeley, G.; Pendleton, A. G. *J. Chem. Soc.* **1952**, 807.
(3) Schubert, W. M.; Latourette, H. K. *J. Am. Chem. Soc.* **1952**, *74*, 1829.
(4) Agranat, I.; Shih, Y. S.; Bentor, Y. *J. Am. Chem. Soc.* **1974**, *96*, 1259.
(5) Agranat, I.; Bentor, Y.; Shih, Y. S. *J. Am. Chem. Soc.* **1977**, *99*, 7068.

0022-3263/83/1948-3360$01.50/0

Table I. Nafion-H-Catalyzed Deacetylation of Aromatic Ketones

ketone	temp, °C	time, h	solvent	product(s) yield,[a] %
 1	78–80	1		 6 (98)
1	98–100	2	toluene	6 (99)
 2	98–100	12	anisole	 7 (99, 80[b])
2	98–100	2	toluene	7 (99)
 3	98–100	12	toluene	 8 (61) +  9 (26)
 4	100	12	anisole	 10 (56) +  11 (1)
 5	100	12	toluene	 12 (95)
5	100	4	toluene	12 (35)

[a] Based on GLC analysis. [b] Isolated yield.

More recently, Gore et al. found acyl transfer in activated aromatic ketones. For example, in the presence of 2 molar equiv. of $AlCl_3$, acetyldurene and mesitylene reacted in chloroform solvent to form durene and acetylmesitylene. The mechanism was suggested to be deacetylation, forming acetyl chloride, which then reacetylates mesitylene.[6] Mechanistic studies using ^{14}C-labeled acetyl chloride and acetylmesitylene showed that acetyl exchange catalyzed by $AlCl_3$ occurs via a synchronous reaction involving an ipso complex.[7]

We have previously shown that Nafion-H is an efficient catalyst for acylation of substituted benzenes with aroyl chlorides or anhydrides.[8] In an attempt to explore transfer acetylation reactions catalyzed by Nafion-H, we have found that whereas the removal of acetyl function occurs from polymethylacetophenones or 9-acetylanthracene over Nafion-H under mild conditions, transacetylation is not a competing process. The yield of acetylanisole or acetyltoluene, even with a 10-fold excess of anisole or toluene, was found to be only 1–2%. The reaction is, therefore, of synthetic value for the deacetylation of activated aryl methyl ketones in a simple one-step process without the need for workup procedures. Table I summarizes the results.

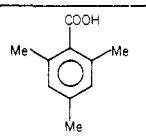
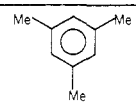
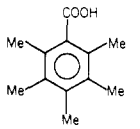
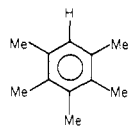
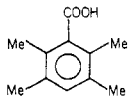
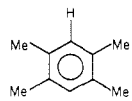
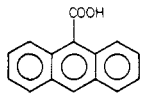
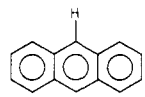
p-Methoxyacetophenone and *p*-methylacetophenone which were the expected products of transacylation themselves did not react with Nafion-H under the reaction conditions, showing that if formed in the reaction mixture, they would have been stable. Favorable ortho steric interaction with the methyl substituents, therefore, seems to provide the driving force for the observed deacetylations. We have also found that peri interactions in 9-acetylanthracene are sufficient activators to allow the removal of the acetyl group by refluxing with Nafion-H in toluene. In general, the yields depend on the reaction time and the amount of Nafion-H used. Generally the reactions proceed to completion upon overnight refluxing.

The intermediate formation of ketene has been previously proposed in the reaction of acetyl chloride and triflic acid, but it could not be directly observed.[9] In the unsuccessful reaction of acetyl chloride with aromatic compounds over Nafion-H, we previously detected diketene formation.[8] When a small amount of ethanol was added to the Nafion-H-promoted deacetylation mixture of acetylmesitylene in toluene as the solvent, ethyl acetate formation was detected by GLC and confirmed by coinjecting an authentic sample. It was also attempted to trap ketene by cyclopentadiene, a suitable ketene trap. The diene, however, polymerized over Nafion-H as soon as the temperature was raised above 50 °C, and thus no conclusive results could be obtained.

Strong support for the suggested mechanism involving ketene in the deacetylation reactions was provided when

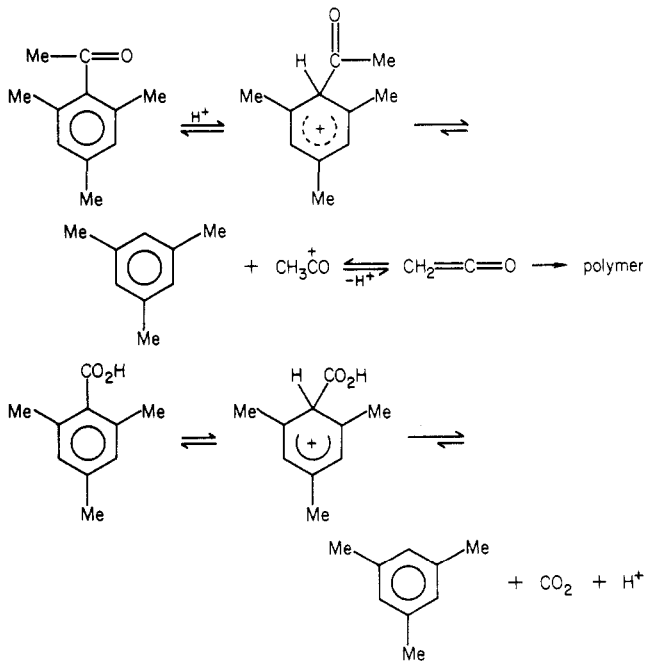
(6) Andreou, A. D.; Bulbulian, R. V.; Gore, P. H. *J. Chem. Res.* **1980**, 225.
(7) Andreou, A. D.; Bulbulian, R. V.; Gore, P. H.; Morris, D. F. C.; Short, E. L. *J. Chem. Soc., Perkin Trans. 2* **1981**, 830.
(8) Olah, G. A.; Malhotra, R.; Narang, S. C.; Olah, J. A. *Synthesis* **1978**, 672.
(9) Effenberger, F.; Epple, G. *Angew. Chem.* **1972**, *84*, 295; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 300.

Table II. Nafion-H-Catalyzed Decarboxylation of Aromatic Carboxylic Acid[a]

acid	temp, °C	solvent	product	yield, %
	100	toluene		80
	100	toluene		~40
	100	toluene		~5
	150	anisole		~25

[a] The reaction time was 12 h in all cases.

Scheme I



benzoylmesitylene was refluxed in anisole over Nafion-H for 12 h. Transbenzoylation occurred to form both mesitylene (38%) and benzoylanisole (32%), together with small amounts (~5%) of methyl- and dimethylanisole products of competing transmethylation under the reactions conditions.

Extending our studies to arenecarboxylic acids we found that polymethylbenzenecarboxylic acids decarboxylate in refluxing toluene over Nafion-H. The effect of a *p*-methyl group in stabilizing the intermediate is reflected when comparing the yields of the decarboxylated products, since mesitylenecarboxylic acid and pentamethylbenzoic acid were decarboxylated more efficiently than 2,3,5,6-tetramethylbenzoic acid (see Table II).

In the anthracene skeleton, favorable peri interactions provide the driving force for decarboxylation, yielding 25% anthracene after overnight refluxing in anisole. In a control experiment anthracene-9-carboxylic acid was heated overnight in refluxing anisole in the absence of the catalyst and showed no decarboxylation.

It is suggested that the deacetylation and decarboxylation reactions proceed via ipso protonation of the substrate. (This process may involve dicationic species as the carbonyl/carboxyl group could also be protonated.) In a subsequent step the functional group leaves or reacts over Nafion-H (to polymerize in case of ketene; see Scheme I).

Experimental Section

Acetylmesitylene, acetyldurene, and acetylpentamethylbenzene were prepared by Friedel–Crafts acetylation of the corresponding methylbenzenes with $CH_3COCl/AlCl_3$ and were purified by fractional distillation or crystallization.

Anthracene-9-carboxylic acid (Aldrich), pentamethylbenzoic acid (Alfa), and 2,3,5,6-tetramethylbenzoic acid (Alfa) had high purity and were used as received.

The solvents were high purity (>98% as determined by GLC) commercial samples.

GLC analysis was performed on a Varian Model 3700 instrument equipped with a capillary column and an on-line automatic integrator.

Proton NMR spectra were recorded on a Varian 60 instrument.

In a typical experiment, to a mixture of the aryl methyl ketone (0.007 mol) and Nafion-H (400–800 mg), was added toluene or anisole (15–20 mL), and the mixture was heated under reflux for a specified period of time. Aliquots were withdrawn for GLC analysis, and the products were characterized on the basis of their retention times by comparison and coinjection with authentic samples.

For acetylpentamethylbenzene the progress of reaction was monitored by TLC with hexane as the solvent. The reaction mixture was cooled to room temperature, filtered and washed repeatedly with ether (5 × 10 mL). The combined filtrate was concentrated, and the residual solid was crystallized with MeOH, to give pentamethylbenzene (80% yield).

For 9-acetylanthracene the progress of reaction was followed by ^1H NMR. The anthracene formed in this reaction was purified by crystallization from hexane.

For arenecarboxylic acids, to the reaction mixture, after filteration of the catalyst, was added a saturated solution of sodium bicarbonate, and the mixture was stirred at room temperature overnight, during which unreacted arenecarboxylic acids were completely dissolved. The organic layer was separated and dried ($MgSO_4$), and the solvent was removed. The decarboxylated arene products were analyzed by GLC and NMR.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. 1, 1667-01-2; 2, 2040-01-9; 3, 15517-58-5; 4, 2142-78-1; 5, 784-04-3; 2,4,6-trimethylbenzoic acid, 480-63-7; 2,3,4,5,6-pentamethylbenzoic acid, 2243-32-5; 2,3,5,6-tetramethylbenzoic acid, 2604-45-7; 9-anthracenecarboxylic acid, 723-62-6; Nafion-H, 63937-00-8.

Reaction of Dimethyl 3-Oxoglutarate with 1,3-Dicarbonyl Compounds

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Dimethyl 3-oxoglutarate, 1, reacts with 1,2-dicarbonyl compounds to produce a variety of cyclic, bicyclic, and

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