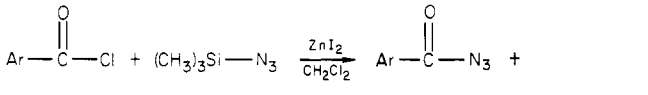
temperature in dichloromethane solution providing the corresponding aroyl azides in high yields (Table I). The reaction (eq 1) does not proceed with out the ZnI_2 catalyst under our conditions.



$(CH_3)_3SiCl$ (1)

The reaction works well with both electron-releasing as well as electron-withdrawing substituents. However, the reaction is much slower with the latter. We feel that the presently developed method is a simple convenient procedure to prepare aroyl azides from readily available trimethylsilyl azide.

Experimental Section

General Procedure. To a stirred mixture of aroyl chloride (20 mmol) and trimethylsilyl azide (20 mmol) in 80 mL of dry dichloromethane under nitrogen at 0 °C is added 20 mg of anhydrous zinc iodide. The stirring is continued at 0 °C for 30 min, and the mixture is slowly warmed to room temperature. The stirring is continued (optimum reaction time is shown in Table I). After the reaction is complete, the mixture is poured into 100 mL of ice-cold water and extracted with dichloromethane (2 × 100 mL). The combined dichloromethane layers are washed once with 5% sodium thiosulfate solution followed by cold water (2 × 100 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent provides aroyl azides which are further purified by recyrstallization or distillation. The reaction with *p*-nitrobenzoyl chloride was carried out with 1 equiv to ZnI_2 catalyst and 2 equiv of trimethylsilyl azide.

Caution: Sufficient care has to be exercised while distilling organic azides because of their explosive nature.[3]

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

Registry No. 4-$(OCH_3)C_6H_4CON_3$, 3532-17-0; 4-$(CH_3)C_6H_4CON_3$, 22693-32-9; 3-$(CH_3)C_6H_4CON_3$, 71313-13-8; $C_6H_5CON_3$, 582-61-6; 4-$BrC_6H_4CON_3$, 14917-59-0; 4-$ClC_6H_4CON_3$, 21368-28-5; 4-$FC_6H_4CON_3$, 16664-09-8; 3-$FC_6H_4CON_3$, 16664-08-7; 4-$(NO_2)C_6H_4CON_3$, 2733-41-7; 4-$(OCH_3)C_6H_4COCl$, 100-07-2; 4-$(CH_3)C_6H_4COCl$, 874-60-2; 3-$(CH_3)C_6H_4COCl$, 1711-06-4; C_6H_5COCl, 98-88-4; 4-BrC_6H_4COCl, 586-75-4; 4-ClC_6H_4COCl, 122-01-0; 4-FC_6H_4COCl, 403-43-0; 3-FC_6H_4COCl, 1711-07-5; 4-$(NO_2)C_6H_4COCl$, 122-04-3; trimethylsilyl azide, 4648-54-8; zinc iodide, 10139-47-6.

Heterogeneous Catalysis by Solid Superacids. 17.[1] Polymeric Perfluorinated Resin Sulfonic Acid (Nafion-H) Catalyzed Fries Rearrangement of Aryl Esters

George A. Olah,* Massoud Arvanaghi, and V. V. Krishnamurthy

Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

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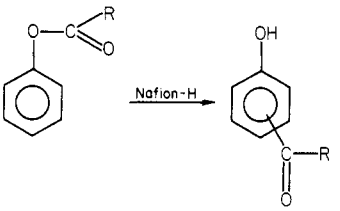
The Lewis acid catalyzed conversion of phenol esters to *o*- or *p*-hydroxyphenyl ketones (Fries reaction) is of substantial synthetic utility.[2] Extensive study has been carried out on the reaction. It has been established that the reaction can be carried out equally well with Lewis acids or Brønsted acids.[3] Catalytic acids used were $AlCl_3$, $HgCl_2$, $SnCl_4$, $FeCl_3$, TsOH,[4] H_3PO_4,[5] HF,[6] BF_3,[7] and the like. Among the wide variety of catalysts, $AlCl_3$ has been most extensively used. Fries rearrangement has been carried out with a number of esters differing in structure in respect to both their phenolic and their carboxylic acid components. The mechanism of the reaction has also been extensively studied in order to establish the role of the catalyst and to determine whether an inter- or intramolecular reaction takes place.[2]

The general method of carrying out Fries reactions is to heat a mixture of the phenolic ester and the catalyst to 80–180 °C, either neat or in a suitable solvent such as $C_6H_5NO_2$, $(CH_2Cl)_2$, C_6H_5Cl, etc. The reactions generally require molar amounts of the catalyst, which forms complexes with the substrate and the product. A workup consequently is needed to decompose these complexes, and the catalyst is usually nonrecoverable.

We report now a much improved, convenient way to carry out the Fries rearrangement of phenol esters to hydroxyphenyl ketones in the presence of Nafion-H,[8] a solid superacidic resin sulfonic acid catalyst. Refluxing a solution of the phenol ester in nitrobenzene in the presence of Nafion-H (~5% by weight with respect to the ester) effects smooth conversion to the corresponding hydroxyphenyl ketones (eq 1). The reaction is general for phenol



(1)

esters of aromatic carboxylic acids,[9,10] and the results are summarized in Table I.

The workup of the reaction mixture is extremely simple, involving filteration of the solid catalyst (which can be reused after simple regeneration), extracting the phenolic ketones into a solution of 10% NaOH, and neutralizing the basic solution with acid. The present method provides excellent yields, an easy workup for the isolation of the product, and ready regeneration of the catalyst without loss of activity. Moreover, only a catalytic amount of catalyst is needed instead of the usual stoichiometric quantity of the conventional Lewis acids. Among the different solvents tried, nitrobenzene was found to be the most suitable for the reaction.

(1) For part 16, see: Olah, G. A.; Mehrotra, A. K. *Synthesis* **1982**, 962.

(2) For a review see: Gerecs, A. In "Friedel–Crafts and Related Reactions"; Olah, G. A., Ed.; Interscience: New York, 1964; Vol. III, p 499.

(3) d'Ans, J.; Limmer, H. *Ber.* **1952**, *85*, 585.

(4) U.S. Pat. 2763691, 1957; *Chem. Abstr.* **1957**, *51*, 8791.

(5) Snyder, H. R.; Elston, C. T. *J. Am. Chem. Soc.* **1955**, *77*, 364.

(6) Darm, O.; Wylius, A. *Justus Liebigs Ann. Chem.* **1954**, *587*, 1.

(7) Kindler, K.; Oelschlager, H. *Ber.* **1954**, *87*, 194.

(8) Nafion is the trade name of the Du Pont Co. for a commercially available perfluorinated resin sulfonic acid ionomer, generally in the form of the potassium salt. Its activation to the H form from the commercial potassium salt and use as a heterogeneous acid catalyst is described in our preceding work (ref 1 and references given therein).

(9) Our attempt to use this procedure for acetate esters was unsuccessful probably due to the formation of ketene under these conditions.[10]

(10) Olah, G. A.; Malhotra, R.; Narang, S. C.; Olah, J. A. *Synthesis* **1978**, 672.

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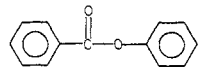
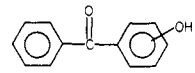
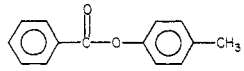
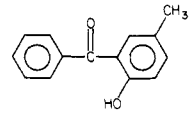
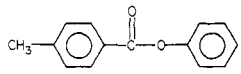
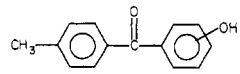
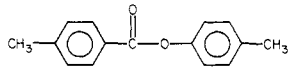
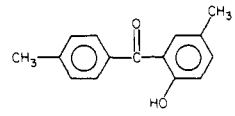
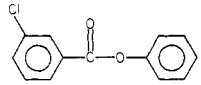
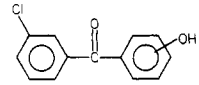
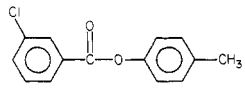
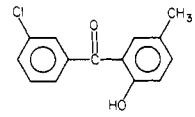
Table I. Fries Rearrangement over Nafion-H Catalyst

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

George A. Olah,* Khosrow Laali, and Ashok K. Mehrotra

Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661

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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.

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