was added slowly a solution of the hydrocarbon (20 mmol) in 10 mL of CH_2Cl_2 with continuous stirring. After the addition the reaction was stirred at room temperature. On completion of the reaction it was poured into ice–water and extracted with ether (2 × 100 mL). The organic layer was washed successively with water, with $NaHCO_3$ solution, and finally with brine solution and dried over anhydrous $MgSO_4$. Removal of solvent gave excellent yields of fluorohydrocarbons which were crystallized with petroleum ether–chloroform solvent and characterized by their physical and spectral data (Table I).

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

Registry No. **1a**, 281-23-2; **1c**, 7575-82-8; **1d**, 2292-79-7; **1e**, 519-73-3; **2a**, 768-92-3; **2d**, 77052-09-6; **2e**, 427-36-1; $NO^+BF_4^-$, 14635-75-7; PPHF, 62778-11-4; isobutane, 75-28-5; isopentane, 78-78-4; methylcyclopentane, 96-37-7; isopropylbenzene, 98-82-8; cyclohexylbenzene, 827-52-1.

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(12) **Caution:** Proper precautions must be taken when handling anhydrous hydrogen fluoride and PPHF. Hydrogen fluoride is extremely corrosive to human tissue, contact resulting in painful, slow-healing burns. Laboratory work with HF should be conducted only in an efficient hood, with the operator wearing a full-face shield and protective clothing. Hydrogen fluoride burns should be immediately treated first with prolonged rinsing with cold water followed by soft, bulky dressings liberally soaked with iced benzalkonium chloride (Zephiran or Hyamine) that may be applied up to 1–4 h.

Zinc Iodide Catalyzed Preparation of Aroyl Azides from Aroyl Chlorides and Trimethylsilyl Azide[1]

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Acid azides are important intermediates as they undergo Curtius rearrangement leading to isocyanates.[2] Isocyanates are generally prepared[2] in a one-pot procedure by treating the acid chloride with ammonium or metal azide without isolating the intermediate acid azide. Although alkanoyl azides are generally unstable and explode on heating, the corresponding aroyl azides are thermally stable and can be isolated.[3] However, the preparation of aroyl azides involves a three-step sequence starting from an aryl ester.[4]

Trimethylsilyl azide reacts with azide chlorides under reflux to give the corresponding isocyanates directly.[5] No attempt has been made thus far to isolate the intermediate acid azides. We report now that aroyl chlorides react with trimethylsilyl azide under zinc iodide catalysis at room

Table I. Zinc Iodide Catalyzed Preparation of Aroyl Azides from Aroyl Chloride and Trimethylsilyl Azide

aroyl azide	rxn time, h	yield,[a] %	mp,[b] (bp/mmHg), °C	lit.[6] mp (bp/mmHg), °C	^{13}C NMR[c] C=O	C_1	C_2	C_3	C_4	C_5	C_6	others
4-$(OCH_3)C_6H_4CON_3$	3	96	70–71	70–71	171.6	123.2	131.7	114.0	164.7	114.0	131.7	55.6 (OCH_3)
4-$(CH_3)C_6H_4CON_3$	3	84	32–33	35	172.6	127.6	129.0	128.9	144.9	128.9	129.0	21.1 (CH_3)
3-$(CH_3)C_6H_4CON_3$	3	93	*d*		172.0	130.4	134.8	138.3	129.7	126.4	128.3	20.8 (CH_3)
$C_6H_5CON_3$	3	95	25–27	27	172.3	130.6	129.4	128.6	134.3	128.6	129.4	
4-$BrC_6H_4CON_3$	5	86	48	47	171.5	129.3	131.9	130.7	129.6	130.7	131.9	
4-$ClC_6H_4CON_3$	3	95	39–42	43	171.5	132.7	130.7	129.0	140.9	129.0	130.7	
4-$FC_6H_4CON_3$	30	85	(72/1.0)		171.0	126.8	132.0 ($^3J_{C-F}$ = 9.8 Hz)	115.6 ($^2J_{C-F}$ = 22.0 Hz)	166.5 ($^1J_{C-F}$ = 255.6 Hz)	115.6 ($^2J_{C-F}$ = 22.0 Hz)	132.0 ($^3J_{C-F}$ = 9.8 Hz)	
3-$FC_6H_4CON_3$	34	94	(74–77/1.0)		171.2 ($^4J_{C-F}$ = 3.2 Hz)	132.6 ($^3J_{C-F}$ = 7.3 Hz)	121.3 ($^2J_{C-F}$ = 22.0 Hz)	162.5 ($^1J_{C-F}$ = 247.9 Hz)	116.1 ($^2J_{C-F}$ = 23.2 Hz)	130.3 ($^3J_{C-F}$ = 7.3 Hz)	125.1 ($^4J_{C-F}$ = 3.3 Hz)	
4-$(NO_2)C_6H_4CON_3$	72	83	64–66	65	170.7	123.9	130.4	123.7	151.4	123.7	130.4	

[a] Purity confirmed by ^1H, ^{13}C NMR, and IR analysis. [b] Melting point and boiling points are uncorrected. [c] In $CDCl_3$ solution at 24 or 37 °C. Chemical shifts are in parts per million from tetramethylsilane. [d] Decomposes upon distillation (to an isocyanate via Curtius rearrangement).

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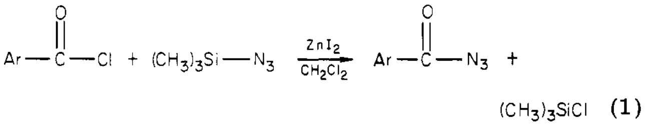
temperature in dichloromethane solution providing the corresponding aroyl azides in high yields (Table I). The reaction (eq 1) does not proceed with out the ZnI_2 catalyst under our conditions.



$$\mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}Cl + (CH_3)_3Si{-}N_3 \xrightarrow[CH_2Cl_2]{ZnI_2} Ar{-}\overset{O}{\overset{\|}{C}}{-}N_3 + (CH_3)_3SiCl} \quad (1)$$

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

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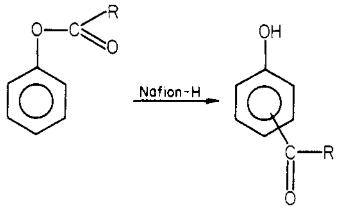
The Lewis acid catalyzed conversion of phenol esters to *o*- or *p*-hydroxyphenyl ketones (Fries reaction) is of substantial synthetic utility.[2] Extensive study has been carried out on the reaction. It has been established that the reaction can be carried out equally well with Lewis acids or Brønsted 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 esters of aromatic carboxylic acids,[9,10] and the results are summarized in Table I.



(1)

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.

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[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]

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