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Highly Efficient Dinitration of Aromatic Compounds in Fluorous Media using Ytterbium Perfluorooctanesulfonate and Perfluorooctanesulfonic Acid as Catalysts

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Abstract: Ytterbium perfluorooctanesulfonate [Yb(OPf)₃] and perfluorooctanesulfonic acid [PFOH] catalyze the highly efficient dinitration of toluene, benzene, benzyl chloride, and chlorobenzene in fluorous media. Notably the process produces almost no waste acid, as opposed to the traditional case. The fluorous phase-containing catalyst could be easily and efficiently recovered for reuse by simple phase separation.

Keywords: Dinitration, fluorous biphasic catalysis, fluorous solvents, perfluorooctanesulfonic acid, ytterbium perfluorooctanesulfonate

Nitration is one of the key processes in synthetic chemistry and is widely used industrially.^[1,2] However, nitration in a manufacturing process requires the use of potent mixtures of concentrated or fuming nitric acid with sulfuric acid leading to excessive acid waste streams and added expense. Although a lot of catalysts or catalytic systems that complete the nitration by catalytic use have been reported, subjects are limited to mononitration in most cases. Thus, development of more efficient and powerful catalysts is strongly demanded for dinitration.^[3] Recently, it was found that ytterbium perfluorooctanesulfonates [Yb(OPf)₃] can catalyze the mononitration of aromatic compounds in moderate yield using concentrated nitric acid in fluorous

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solvents.^[4] Yuan et al. used MCM-41-supported metal bis[(perfluoroalkyl)sulfonyl]imides $[M(\text{NPF}_2)_n]$ as catalysts for nitration of aromatic compounds.^[5] A novel fluorinated catalyst for nitration, cyclic trimeric perfluoro-*o*-phenylene-mercury $[(o\text{-C}_6\text{F}_4\text{Hg})_3]$, was reported by Zaraisky et al.^[6] Crampton and coworkers reported that perfluorocarbons can be used effectively as solvents and bulking agents in the dinitration of aromatic compounds with nitric acid or dinitrogen pentoxide to yield highly nitrated products.^[7] However, this dinitration required at least 5 equiv nitric acid or dinitrogen pentoxide, in addition to rather drastic reaction conditions and tedious workup procedures required when using dinitrogen pentoxide as a nitration reagent. Inspired by the recent work on the Friedel–Crafts acylation of unactivated benzenes catalyzed by $\text{Yb}(\text{OPf})_3$ with the coexistence of perfluorooctanesulfonic acid [PFOH] using perfluorocarbon as solvent,^[8] we have applied this catalytic system to the dinitration of aromatic compounds, such as toluene, benzene, benzyl chloride, and chlorobenzene. As expected high yields of the corresponding dinitrobenzenes and the robustness of the catalytic system for recycling using by simple phase-separation were obtained. We report herein the work on this new application of the catalytic system.

The dinitration of toluene was first carried out in various fluorous using slightly excess 95% nitric acid as the nitration reagent. Based on the general concept of fluorous phase chemistry,^[9] we also used hexane as a cosolvent for the nitration. It was found that upon heating at 60°C, the organic phase is miscible with fluorous phase, and the nitration became a biphasic reaction (top layer is the nitric acid; bottom layer is the fluorous solvent with aromatic compound). Much lower yields of dinitration were obtained in the presence of PFOH or $\text{Yb}(\text{OPf})_3$ (5% and 8% yields, respectively). In addition, a $\text{Yb}(\text{OPf})_3$ -PFOH catalyst loading of only 0.5 mol% was required to produce quantitative yields of dinitrotoluene. The ratio of 2,4-isomer to 2,6-isomer in the production is generally ca. 4:1, which is typical for nitronium ion nitrations.^[7] Other lanthanide perflate catalytic systems were also examined for the nitration in the same reaction conditions. We found that $\text{Sc}(\text{OPf})_3$ -PFOH had a similar catalytic activity for the reaction with a quantitative conversion to dinitro product over 4 h, whereas the systems containing other lanthanide perflates, namely $\text{La}(\text{OPf})_3$ or $\text{Eu}(\text{OPf})_3$, yielded dinitrotoluene in 46% and 59%, respectively. This is ascribed to the higher Lewis acidity of $\text{Yb}(\text{OPf})_3$ and $\text{Sc}(\text{OPf})_3$ than those of other lanthanide perflates. When using perfluorotoluene (C_7F_8) and perfluoromethylcyclohexane (C_7F_{14}) as fluorous solvents in $\text{Yb}(\text{OPf})_3$ -PFOH catalyzed cases, the nitration also proceeded smoothly to give the desired product. However, perfluorotoluene is in fact miscible with reaction aromatic substrates at room temperature. Thus, it is impossible to recover the fluorous phase by phaseseparation. In addition, it was found that during repeated nitration reactions the loss of fluorous solvent is very serious when using perfluoromethylcyclohexane (C_7F_{14}) as a fluorous solvent because it is very volatile (bp 76°C).

Thus, to seek out a practical and economical dinitration, we decided to use relatively cheap and similarly active Yb(OPf)₃-PFOH as catalysts and perfluorodecalin (C₁₀F₁₈, *cis*- and *trans*-mixture) as the fluorosolvent for the dinitration of other aromatic compounds. The results are summarized in Table 1. As shown in Table 1, when 2-nitrotoluene and 4-nitrotoluene were performed as substrates, the dinitration was completed in a shorter time. Although the reaction became slower in nitration of benzene, the advantages of the catalytic system were still clear: benzene gave a quantitative conversion to the dinitrobenzene in 16 h, as opposed to the uncatalyzed case, which proceeded to only 2% conversion. As to the isomers of product of benzene, small proportions of 1,2- and 1,4-dinitrobenzene were formed in addition to the major 1,3-isomer. As an extension of the present work, we have investigated the dinitration of benzyl chloride and chlorobenzene under similar conditions. The reaction of benzyl chloride gave 2,4- and 2,6-dinitrobenzyl chlorides in an 86:14 ratio. In the case of chlorobenzene, the reaction produced a 2,4-/2,6-dinitrochlorobenzene in a ratio of 97:3, which is much higher than the mixed acid nitration case with the ratio of 90:10. The reaction was unsuccessful for phenol and benzyl alcohol, which presumably suffered complications due to competing oxidation of the hydroxy.

Table 1. Summary of the reactions for dinitration of aromatics^a

Substrate	Time (h)	Isomers of product/ composition (%) ^b	Isomers of product/ composition (%) ^b	Isomers of product/ composition (%) ^b
Toluene	4	2,4- (80)	2,6- (18)	Others (2)
Toluene ^c	4	2,4- (84)	2,6- (16)	
Toluene ^d	4	2,4- (81)	2,6- (16)	Others (3)
2-Nitrotoluene	2.5	2,4- (68)	2,6- (32)	
4-Nitrotoluene	2.5	2,4- (>99)	2,6- (<1)	
Benzene	16	1,3- (90)	1,4- (8)	Others (2)
Benzene ^e	16	1,3- (2)	1,4- (-)	
Benzyl chloride	8	2,4- (86)	2,6- (14)	
Chlorobenzene	18	2,4- (97)	2,6- (3)	

^aReaction conditions for dinitration: substrate (0.0025 mol), 2.1 equiv. 95% HNO₃, Yb(OPf)₃ (0.5 mol%), PFOH (0.5 mol%), perfluorodecalin (5 mL), hexane (3 mL), 60°C. Reaction conditions for mononitration: substrate (0.0025 mol), 1.1 equiv. 95% HNO₃, Yb(OPf)₃ (0.5 mol%), PFOH (0.5 mol%), perfluorodecalin (5 mL), hexane (3 mL), 60°C. Conversion of substrate was more than 99.5% by GC analysis.

^bComposition was determined by GC using an internal standard method.

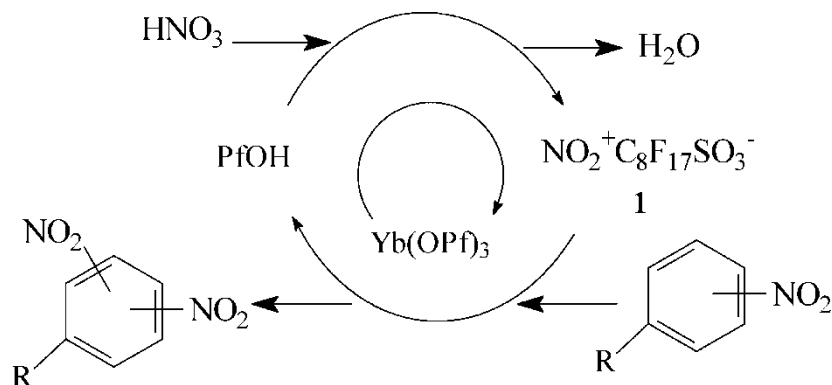
^{c,d}Perfluorotoluene and perfluoromethylcyclohexane as fluorosolvents respectively.

^eUncatalyzed case.

When the reaction was finished, the reaction mixture was cooled to room temperature. The fluorous phase with $\text{Yb}(\text{OPf})_3$ and PfOH catalysts can separate from the organic layer and return to the bottom layer. Use of fluorous phase, recycled without purification, was equally effective. The dinitrations of toluene under the conditions mentioned previously were run for three consecutive cycles, furnishing the corresponding product with 99, 97, and 96% yields. Based on the ^{19}F NMR and UV-vis spectroscopic data and GC-MS, no loss of catalyst or fluorous solvent to the organic and water phases can be detected. However, we found that the loss of PfOH leaking to the water phase become obvious when the volume ratio of fluorous phase to water phase decreased greatly. The results of ^{19}F NMR and UV-vis showed that the loss of PfOH was increased from 0.1% to 8.9% with the ratio mentioned previously decreasing from 10:1 to 1:1. Thus, controlling the high volume ratio of fluorous phase to water phase was important strategy for the use of this novel catalytic system in nitration.

Finally, the assumed catalytic cycle is shown in Scheme 1. A key highly efficient nitration agent is proposed as nitroperflate **1**,^[10] which reacts even with nitro aromatic compounds to afford the corresponding dinitrobenzenes, accompanied by regeneration of PfOH . $\text{Yb}(\text{OPf})_3$ is assumed to catalyze the nitration involving **1** because of its complexation with **1**, which easily makes NO_2^+ release from the ion pair **1**. In addition, $\text{Yb}(\text{OPf})_3$ -promoted generation of **1** is proposed because of its high oxophilicity in the catalytic cycle.

In conclusion, the $\text{Yb}(\text{OPf})_3$ - PfOH -PFC system can be considered the most attractive alternative to existing heterogeneous catalytic systems for dinitration of toluene, benzene, benzyl chloride, and chlorobenzene, and this report may open the door to solve the long-term dinitration of aromatic compounds problem, such as treatment of excessive sulfuric acid and waste water.



Scheme 1. Assumed catalytic cycle for the dinitration.

EXPERIMENTAL

Typical Procedure

A mixture of Yb(OPf)₃ (21 mg, 0.012 mmol), PFOH (6 mg, 0.012 mmol), toluene (0.26 ml, 2.5 mmol), hexane (3 ml), perfluorodecalin (C₁₀F₁₈, *cis*- and *trans*-mixture, 5 ml) and 95% HNO₃ (0.22 ml) was stirred at 60°C for 4 h. Then, the fluoruous layer on the bottom was separated for the next nitration. The reaction mixture (organic phase) was treated with the usual workup. Conversion and composition were determined by GC or GC-MS using an internal standard method.

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