Journal of Fluorine Chemistry 160 (2014) 77–81

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Catalytic application of fluorous silica gel in Fries rearrangement

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ARTICLE INFO

Article history:
Received 27 November 2013
Received in revised form 5 January 2014
Accepted 8 January 2014
Available online 20 January 2014

Keywords:
Fluorous silica gel (Fluoro Flash™)
Fries rearrangement
Aryl esters.

ABSTRACT

Commercially available fluorous silica gel (Fluoro Flash™) with no further post-modification was successfully investigated and applied merely as a catalyst in Fries rearrangement of various aryl esters under solvent free conditions in 4 h and optimized temperatures. In addition to good yields and recyclability of the catalyst, toxicity of reaction medium, by-products, and wastes were minimized. Also, low catalyst loading was another advantage of this methodology.

1. Introduction

The original Fries rearrangement was published by Fries and Finck more than 100 years ago in which *p*-cresyl chloroacetate was heated to 140 °C in the presence of $AlCl_3$ [1]. This rearrangement is a significant synthetic strategy for the preparation of biologically and medicinally interesting acylated scaffolds [2,3]. Fries rearrangement has been reported with many homogenous catalysts such as polyphosphoric acid, $MeSO_3H/POCl_3$, montmorillonite clays, $Hf(OTf)_4$, $ZrCl_4$, $Sc(OTf)_3$, and $TiCl_4$ [4–10]. These procedures require a prohibitively large amount of a Lewis or Brønsted acid (e.g., $AlCl_3$ or H_2SO_4) which result in larger amount of waste materials and cause to a strong corrosion [11,12]. In addition, homogenous catalysts are unrecoverable. To overcome this problem, much effort has been put into developing heterogeneous catalysts in Fries rearrangement such as solid catalysts [11–14]. Heteropolyacids (HPAs), such as $H_3PW_{12}O_{40}$ (PW), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW), H-beta, and ion-exchange resins (Amberlyst-15, Nafion-117) are examples of heterogeneous solid acid catalysts for Fries reaction [15–17].

In recent years, fluorous silica gel [18] (FSG) has been successfully applied as a solid support for heterogeneous catalyst in the organic reactions such as carbon-carbon couplings [19,21], protection [22], *N*-formylation [23]. However, FSG itself can be used merely without any post-modifications due to its highly active surface by perfluoroalkyl chains bonded to the surface of silica gel [24]. There have been many reports which confirm the catalytic activity of fluorous compounds such as fluorous solvents and their roles when dispersed on silica solid supports [25–28]. Therefore, these supports can be either a potent candidate in catalyzing the reactions. However, application of mere FSGs are only limited to extraction and separation in synthetic chemistry [24]. In the present study, we have introduced the FSG (Fluoro Flash™) as a recoverable, highly active, and economical catalyst for the Fries rearrangement.

2. Results and discussion

Over the last decade, development of FSGs applications have been enhanced as absorbents and catalytic support [20–24,29]. Although, FSGs are suitable supports in various organic reactions due to exceptional nature of fluorous compounds, their modifications are sometimes difficult, costly, or time consuming. These disadvantages are drawbacks of their large scale production and industrialization. Therefore, development of available and low cost catalysts as potent as fluorous-tagged catalysts which are immobilized on the FSG surface (e.g. efficiency, recyclability, etc.) can surpass these problems. Hence, we studied and developed the catalytic application of unmodified FSG, which is available under the commercial name of Fluoro Flash™, in Fries rearrangement of various aryl esters. Mechanism of rearrangement when catalyzed by FSG is not clear yet. However, it can be proposed that silica surface due to having perfluoroalkyl chains on the surface tends to share its fluorine atoms in hydrogen bonding which affect on the acidity of silanol groups and cause to increase their O–H acidity [30]. In addition, perfluoroakyl chains may directly undergo a strong interaction with reactants (Scheme 1).

Results showed the FSG as a green, recyclable, highly efficient and readily available catalyst in the present process. To show the unique catalytic behavior of FSG, the non-fluorinated silica gel (SG) and FSG were compared in Fries rearrangement by a model

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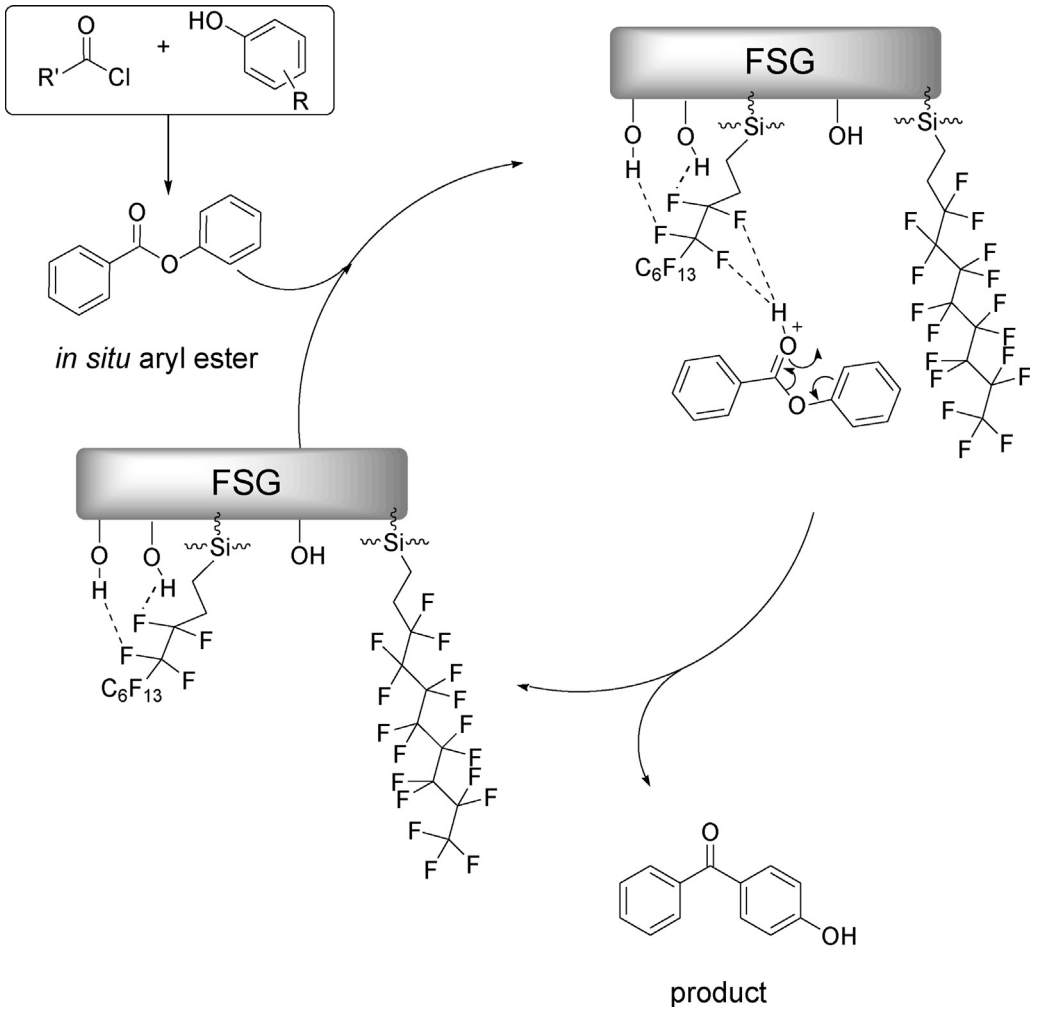
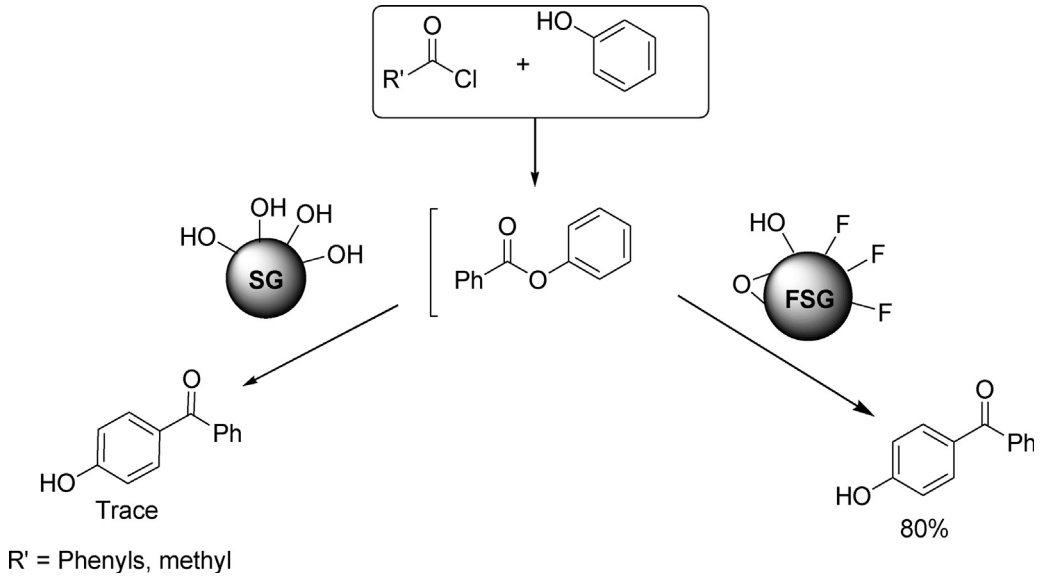
http://dx.doi.org/10.1016/j.jfluchem.2014.01.005



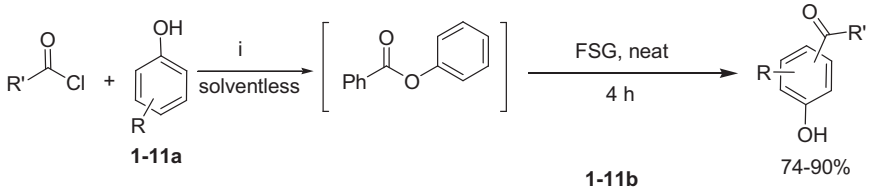
Scheme 1. Proposed mechanism for surface interaction of FSG with reactant.

reaction (Entry 1) under the similar conditions. The results showed no reaction when catalyzed by SG (Scheme 2). After sufficient studies, the optimal conditions for each substrate and the rearranged product are shown in Table 1. During the synthesis of diverse derivatives of aryl esters, diacylated biphenols showed a different behavior in Fries rearrangement and only one of the acyl groups underwent migration and another acetyl group hydrolyzed (Entry 9–11) [31].



Scheme 2. Fries rearrangement of aryl ester in the presence SG and FSG.

Table 1
Optimal conditions for Fries rearrangement of aryl esters catalyzed by FSG.



1-11a **1-11b**

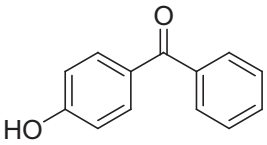
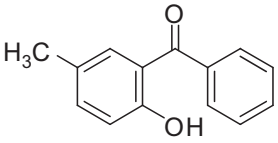
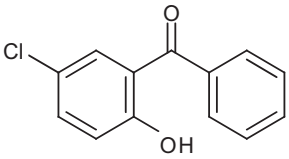
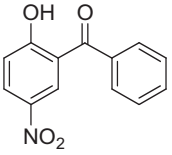
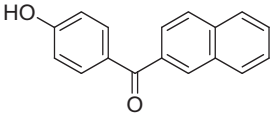
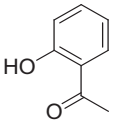
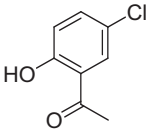
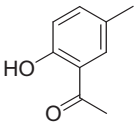
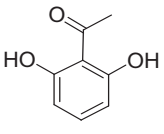
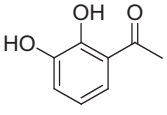
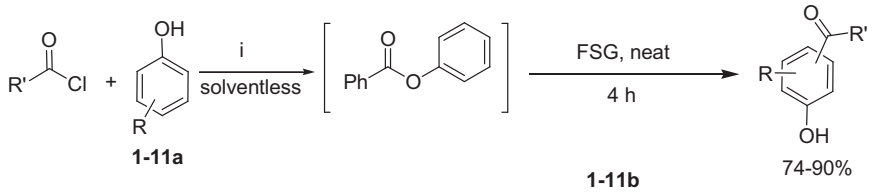
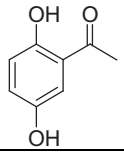
Entry[a]	*R*′	*R*	Product	Yield (%)	Temperature (°C)
1	Ph	H		80	80
2	Ph	4-Me		85	80
3	Ph	4-Cl		85	80
4	Ph	4-NO_2		–	80–120
5	β-naphtyl	H		75	80
6	Me	H		85	80
7	Me	4-Cl		90	80
8	Me	4-Me		74	80
9	Me	3-OH		77	80
10	Me	2-OH		77	80

Table 1 (*Continued*)



Entry[a]	*R*′	*R*	Product	Yield (%)	Temperature (°C)
11	Me	4-OH		80	80

[a] Reaction conditions: (i) Catalyst free, 30 min, (ii) 10 mmol substrate and 1 g FSG was reacted in solvent free conditions in 4 h.

Recyclability studies based on the yield of model reaction (Entry 1) was achieved. As shown in Table 2, this catalyst has been recycled and used at least for six times with low decrease in the yield.

Solvent effect on the reaction was also studied. Several solvents such as THF, *n*-hexane, ethanol, water, and dioxane were tested with one model reaction under the same conditions (Entry 1). In this case, the reaction conditions were the same as discussed in 4.2 except that FSG was suspended with 2 mL of every solvent and then added to the mixture of reaction. Due to the fact that the most efficient solvent yield was close to neat conditions, therefore solvent free method was selected as optimal conditions (Table 3). Obtained results from GC chromatography showed that when water was used as the solvent, the major amount (~>97) of aryl esters convert to product with good yield and remaining substrate to hydrolyzed form of corresponding acid and phenol, and only few amount of substrate stayed unreacted. However, when neat approach was incorporated into Fries rearrangement, no more hydrolysis occurred and therefore unreacted substrate remained intact. It was one of our reasons for selecting neat conditions. Temperature was optimized by the model reaction under the similar conditions for Fries rearrangement. According to this investigation, 80 °C was optimized temperature for Fries rearrangement (Table 4).

Table 2
Results of 8 times recycle for Fries rearrangement.

Number of recycles	Yield (%)
1	80
2	80
3	80
4	80
5	79
6	79
7	75
8	75

Table 3
Solvent effect study on the Fries rearrangement.

Solvent	Yield
THF	64
n-Hexane	12
Diethylether	55
Ethanol	75
Water	51
Dioxane	68
–	80

Table 4
Temperature optimization of Fries rearrangement.

Temperature (°C)	Yield
Rt	64
50	66
60	70
80	80
90	80
100	80

3. Conclusion

According to recent advances in the properties of fluorinated materials such as their solvents and fluorous supports, etc., the present work features the potential catalytic activity of unmodified FSG in Fries rearrangement. In addition, simplicity, reusability, low cost of preparation, and high efficiency of this catalyst led to unique catalyst among the other similar catalysts. It can also be concluded that discovering catalytic activity of FSG may be an impact in studying it for further similar organic reactions.

4. Experimental

4.1. Chemicals and apparatus

All reagents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Melting points were measured by an Electrothermal 9100 apparatus. Progress of reactions was monitored by thin layer chromatography (TLC). IR spectra were recorded on Bruker, Vector 22 spectrometer; absorbance is reported in cm^{-1}. ^1H NMR spectra were run on Bruker DRX-500 AVANCE spectrometer at 500 MHz in $CDCl_3$. Mass analyses were achieved by Fison Instruments TIRO 1000-GC 8000-GC/MS.

4.2. General procedure for Fries rearrangement and catalyst preparation

Catalyst (FSG) was purchased from Fluorous Technologies Inc. and used without further purification. Its synthesis procedure is reported by Curran et al. [24]. General procedure for Fries rearrangement was done by adding FSG to aryl ester at the ambient temperatures. Before adding FSG to reaction mixture, aryl esters

were obtained by in situ formation through the reaction of acyl chloride derivatives and phenol derivatives. Thus, to a 100 ml round bottom flask stirring by a magnetic bar 10 mmol of phenols was added and then, 10 mmol of acyl chloride derivatives (for catechols 20 mmol) was added dropwise and allowed to react at room temperature. After 30 min, temperature was raised to remove HCl from reaction mixture. Then 1 g of FSG was added to reaction mixture at ambient temperature. After 4 h heating at appropriate temperature in oil bath, the reaction mixture was cooled to room temperature and washed with dichloromethane. The catalyst was separated by filtration. The solvent was removed by rotary evaporator and resulting mixture was separated by column chromatography (stationary phase: silica-gel, eluent:hexane:ethyl acetate) and purified by recrystallization. All isolated products successfully gave related spectral data of IR, NMR, and mass spectrometers.

(1) (4-*hydroxyphenyl*)(*phenyl*)*methanone* (1b) [32]: mp. 132–134 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.1 (s, 1H), 6.95 (m, 2H), 7.50 (m, 1H), 7.59 (m, 1H), 7.78 (m, 2H), 7.80 (m, 2H); IR (KBr, υ, cm^{-1}): 31040, 3066, 1630, 1600; MS *m/z* 198 (M^+), 121, 105, 93, 77.

(2) (2-*hydroxy*-5-*methylphenyl*)(*phenyl*)*methanone* (2b) [33]: mp 83–85 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.29 (s, 3H), 7.01 (d, 1H, J = 8.44 Hz), 7.35 (dd, 1H, J_1 = 8.44 Hz, J_2 = 2.1 Hz), 7.39 (d, 1H, J = 1.41 Hz), 7.53 (m, 2H), 7.61 (m, 1H), 7.70 (dd, 1H, J_1 = 6.50 Hz, J_2 = 2.00 Hz), 11.89 (s, 1H); IR (KBr, υ, cm^{-1}): 3421, 3055, 2914, 1626, 1597; MS, *m/z*: 212 (M^+), 211, 135, 105, 77, 27.

(3) (5-*chloro*-2-*hydroxyphenyl*)(*phenyl*)*methanone* (3b) [34]: mp 84–87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.56 (s, 3H), 6.96 (d, 1H, J = 8.90 Hz), 7.43 (dd, 1H, J_1 = 8.90 Hz, J_2 = 2.56 Hz), 7.71 (d, 1H, J = 2.56 Hz), 12.16 (s, 1H); IR (KBr, υ, cm^{-1}): 3446, 3046, 2926, 1622, 1600; MS, *m/z*: 232 (M^+), 105, 77.

(4) (4-*hydroxyphenyl*)(*naphthalen*-2-*yl*)*methanone* (5b) [35]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20–8.24 (m, 11H); IR (KBr, υ, cm^{-1}): 3338, 3051, 2964, 1612, 1570; MS *m/z* 248 (M^+), 171, 143, 115, 105, 77.

(5) 1-(2-*hydroxyphenyl*)*ethanone* (6b) [36]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.63 (s, 3H), 6.94 (m, 1H), 6.98 (d, 1H, 8.40 Hz), 7.47 (m, 1H), 7.74 (dd, 1H, J_1 = 8.00 Hz, J_2 = 1.40 Hz), 12.28 (s, 1H); (KBr, υ, cm^{-1}): 3500–2500, 3049, 2976, 1641; MS, *m/z*: 136 (M^+), 121, 93, 65, 43.

(6) 1-(5-*chloro*-2-*hydroxyphenyl*)*ethanone* (7b) [37]: mp 51 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.65 (s, 3H), 6.96 (d, 1H, J = 8.90 Hz), 7.44 (dd, 1H, J_1 = 8.90 Hz, J_2 = 2.50 Hz), 7.71 (d, 1H, J = 2.50 Hz), 12.16 (s, 1H); IR (KBr, υ, cm^{-1}): 3500–2500, 3082, 2926, 1633, 1600; MS, *m/z*: 170 (M^+), 155, 127, 77, 43, 18, 15.

(7) 1-(2,6-*dihydroxyphenyl*)*ethanone* (8b) [38,39]: mp 155–157 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.59 (s, 3H), 5.70 (s, 1H), 6.41 (m, 2H), 7.66 (1H, d, J = 8.58 Hz), 12.67 (s, 1H); IR (KBr, υ, cm^{-1}): 3298, 1610; MS, *m/z*: 152 (M^+), 137, 136, 109, 81, 43, 42, 29.

(8) 1-(2,3-*dihydroxyphenyl*)*ethanone* (9b) [40]: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.78 (s, 3H), 6.42 (d, 2H), 7.25 (m, 1H); IR (KBr, υ, cm^{-1}): 3304, 3013, 2931, 1630, 1591; MS *m/z*: 152 (M^+), 137, 109, 81, 77, 43, 29.

(9) 1-(2,5-*dihydroxyphenyl*)*ethanone* (10b) [41]: mp 97-99 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.60 (s, 3H), 5.5 (s, 1H), 6.83 (d, 1H, J = 8.90 Hz), 7.06 (dd, 1H, J_1 = 8.90 Hz, J_2 = 2.94 Hz), 7.20 (d, 1H, J = 2.94 Hz), 11.75 (s, 1H); IR (KBr, υ, cm^{-1}): 3246, 3057, 2850, 1616, 1577; MS, *m/z*: 152 (M^+), 137, 136, 109, 77, 42, 28, 15.

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