International Journal of Universal Science and Technology
ISSN: **ISSN: 2454-7263** Copyright © Universal Print
Volume No. 03, Issue No. 03, Page No. 130-132 Published: Jan. 2018
Web: www.universalprint.org , Email: ijup@universalprint.org
Title Key: Synthesis and Fries Rearrangement of …

Synthesis and Fries Rearrangement of Phenylchloroacetate by Using Eco-Friendly Solvent Free Catalyst

Gangadhar B. Gundlewad[1] Bhagwan R. Patil[2]

[1]Department of Chemistry, Shri Shivaji College, Parbhani (MS) India
[2]Department of Chemistry, Sharda Mahavidyalaya, Parbhani (MS) India
e-mail gbgundlewd@rediffmail.com

Abstract

The Fries rearrangement of aromatic esters is usually performed in Lewis acid (AlCl3), In the present study the fries rearrangement is extended to phenylchloroacetate to obtain 2-chloro-1-(2-hydroxyphenyl)ethanone under solvent free eco-friendly catalyst.

Keywords: Fries rearrangement,PTSA, phenylchloroacetate

1. Introduction

The fries rearrangement of aryl ester, a special case of friedel crafts acylation provides an important route for the synthesis of aromatic hydroxyl aryl ketones that find various uses. [1]

Ther rearrangement of aryl ester into hydroxyacetophenone in presence of $AlCl_3$ have been well documented[2,3]. As can be seen from the number of papers which appears in last few years, the fries rearrangement is still a fascinating object of investigation for organic chemist. Thus a wide variety of catalyst such as BCl_3[4], polyphosphoric acid[5], methane sulfonic acid/$POCl_3$[6], montmorollonite clay[7], halfnium trifluoromethansulfonate[8], scandium trifluoromethansulfonate[9], P_2O_5 / SiO_2under microwave[10] , $FeCl_3$[11], Zn powder[12], mesostructured SBA-15 material[13]. But these are corrosive and environment unfriendly catalysts. Thus can leads to violation of several principles of green chemistry.

In the present study the fries rearrangement is extended to phenylchloroacetate to obtain 2-chloro-1-(2-hydroxyphenyl)ethanoneunder solvent free eco-friendly catalyst.

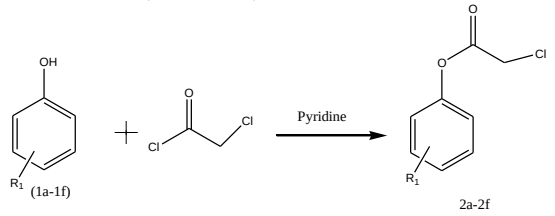
2. Materials andmethods

General: All the chemicals were obtained from E-Merck, India (AR grade) andwere usedwithout further purification. Melting points were taken in an open capillary tube.IRspectra wererecorded on a Shimadzu Dr-8031 instrument. 1H NMR spectra of the synthesizedcompoundswere recorded on a Bruker-Avance(300MHz) and Varian-Gemini (200MHz)spectrophotometerusing CDCl3 solvent and TMS as an the internal standard.

Synthesis of*p*-Toluenesulfonic acid (PTSA).A mixture of pure toluene87g (100ml, 0.95mol)
and concentrated sulfuric acid 37g (20ml, 0.35mol) was gently boiled for 1 hour and cooled, thesolid*p*-toluenesulfonic acid was precipitated out. It was filtered and dried, yield 35 %, m.p.105^0C-106^0C.

International Journal of Universal Science and Technology
ISSN: **ISSN: 2454-7263** Copyright © Universal Print
Volume No. 03, Issue No. 03, Page No. 130-132 Published: Jan. 2018
Web: www.universalprint.org , Email: ijup@universalprint.org
Title Key: Synthesis and Fries Rearrangement of …

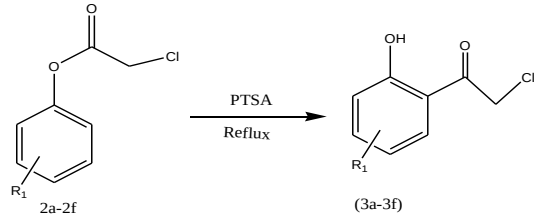
Synthesis of Phenyl chloroacetates. A mixture of phenol (1mol) and drypyridine (10ml) was placed in a 500ml beaker. It was kept in ice bath and chloroacetyl chloride (1.25mol) was added slowly with constant stirring. After completion of reaction (as indicated by TLC) the reaction mixture was poured on amixture of ice cold water and concentrated hydrochloric acid (50ml) and extracted with carbontetrachloride (100ml). The extract was washed successively with water, 10% NaOHsolution andagain with water. It was dried over calcium chloride. The solvent was removed by distillation.(Table**2.1**).



Compound	R	% yield	Solubility in NaOH	B P.
2a	H	72	Insoluble	143
2b	o-CH3	62	insoluble	160
2c	p-CH3	66	insoluble	125
2d	m-CH3	68	insoluble	132
2e	p-Cl	60	insoluble	147
2f	o-CL	63	insoluble	150

Fries rearrangement of Phenyl chloroacetate

Phenyl chloroacetate(0.073mol)was poured in 100 mlround bottom flask containing *p*-toluenesulphonicacid (0.042mol). The reaction mixture washeated on an oil bath at required temperature & time. It was poured on ice cold water with vigorousstirring.*2-chloro-1-(2-hydroxyphenyl)ethanone* was isolated by steam distillation.



Compound	R	Temp.	Time	% yield	M. P.
3a	H	110	1	72	70
3b	o-CH_3	90	1.50	62	67
3c	p-CH_3	110	1.50	66	65
3d	m-CH_3	120	2	68	102
3e	p-Cl	110	2.5	60	107
3f	o-CL	130	2.5	63	72

***Synthesis of 2-chloro-1-(2-hydroxyphenyl)ethanone 3a*IR (KBr.) cm^{-1}**3385 (-OH), 3008 (CH2), 2940 (C-H),1650 (-C=O);**^{1}HNMR ($CDCl_3$)ppm:** -δ 12.05 (s, 1H); 4.63 (s, 2H); 6.50-8.10 (m,4H);**M.S.**- *m/z* -170 $M^{+\cdot}$, *Anal. % Calcd. for*$C_8H_7ClO_2$:C, 56.32; H, 4.14; Cl, 20.78;O, 18.76 Found: C, 56.30; H, 4015; Cl, 20.68; O, 18.77.

***Synthesis of2-chloro-1-(2-hydroxy-3-methylphenyl)ethanone 3b*IR (KBr.) cm^{-1}**3395 (-OH), 3018 (CH2), 2950 (C-H),1670 (-C=O);**^{1}HNMR ($CDCl_3$)ppm:** -δ 12.09 (s, 1H); 4.78 (s, 2H); 2.48 (s, 3H); 6.50-8.10 (m,3H);**M.S.**- *m/z* -184 $M^{+\cdot}$, *Anal. % Calcd. for*$C_9H_9ClO_2$:C, 58.55; H, 4.91; Cl, 19.20; O, 17.32 Found: C, 58.60; H, 4.20; Cl, 19.18; O, 17.33.

***Synthesis of2-chloro-1-(2-hydroxy-5-methylphenyl)ethanone 3c*IR (KBr.) cm^{-1}**3390 (-OH), 3028 (CH2), 2940 (C-H),1665 (-C=O);**^{1}HNMR ($CDCl_3$)ppm:** -δ 12.06 (s, 1H); 4.73 (s, 2H); 2.38 (s, 3H); 6.70 (d, 1H); 7.1 (d, 1H); 7.50 (s,1H);**M.S.**- *m/z* - 184 $M^{+\cdot}$, *Anal. % Calcd. for*$C_9H_9ClO_2$:C, 58.55; H, 4.91; Cl, 19.20;O, 17.33 Found: C, 58.60; H, 4.20; Cl, 19.18; O, 17.32.

***Synthesis of2-chloro-1-(2-hydroxy-4-methylphenyl)ethanone 3d*IR (KBr.) cm^{-1}**3385 (-OH), 3018 (CH2), 2945 (C-H),1668 (-C=O);**^{1}HNMR ($CDCl_3$)ppm:** -δ 12.07 (s, 1H); 4.63 (s, 2H); 2.38 (s, 3H); 6.60 (s, 1H); 6.96 (d, 1H); 7.50 (s,1H);**M.S.**- *m/z* - 184 $M^{+\cdot}$, *Anal. % Calcd. for*$C_9H_9ClO_2$:C, 58.55; H, 4.91; Cl, 19.20; O, 17.33 Found: C, 58.60; H, 4.20; Cl, 19.18; O, 17.34.

***Synthesis of2-chloro-1-(5-chloro-2-hydroxyphenyl)ethanone 3e*IR (KBr.) cm^{-1}**3385 (-OH), 3015 (CH2), 2945 (C-H),1678 (-

International Journal of Universal Science and Technology
ISSN: **ISSN: 2454-7263** Copyright © Universal Print
Volume No. 03, Issue No. 03, Page No. 130-132 Published: Jan. 2018
Web: www.universalprint.org , Email: ijup@universalprint.org
Title Key: Synthesis and Fries Rearrangement of …

C=O);**^{1}HNMR ($CDCl_3$)ppm:** -δ 12.11 (s, 1H); 4.55 (s, 2H); 6.75 (d, 1H); 7.12 (d, 1H); 7.55 (s,1H);**M.S.**- *m/z* - 204 $M^{+\cdot}$, *Anal. % Calcd. for* $C_8H_6Cl_2O_2$:C, 46.86; H, 2.95; Cl, 35.58; O, 15.61 Found: C, 46.87; H, 2.96; Cl, 35.57; O, 15.62.

***Synthesis of2-chloro-1-(3-chloro-2-hydroxyphenyl)ethanone 3f*IR (KBr.) cm^{-1}**3385 (-OH), 3015 (CH2), 2945 (C-H),1678 (-C=O);**^{1}HNMR ($CDCl_3$)ppm:** -δ 12.11 (s, 1H); 4.55 (s, 2H); 6.75 (d, 1H); 7.12 (d, 1H); 7.55 (s,1H);**M.S.**- *m/z* - 204 $M^{+\cdot}$, *Anal. % Calcd. for* $C_8H_6Cl_2O_2$:C, 46.86; H, 2.95; Cl, 35.58; O, 15.61 Found: C, 46.87; H, 2.96; Cl, 35.57; O, 15.62.

3. Results and discussion

The Fries rearrangement was performed at 900-1600C without any solvent using catalyticamount of *p*-toluenesulfonicacid. The yields of products were obtained near about same as thatof with alluminium chloride (AlCl3). The reaction time was also importance, 70% conversion ofphenyl acetates**2a** was achieved within 30 min.at 900-1600C.The ortho/para ratio**3a/4a** was always in favors of the desired compound **3a**. The reactionmay be carried out under optimized temperature, low temperature favors the formation paraproduct and high temperature favors the formation orthoproduct.Thesynthesized compounds have been confirmed on the basis of elemental analysis and spectral data. Itwas found to be veryimportantto use an anhydrous*p*toluenesulfonic acid, as traces ofwater hydrolyze phenyl chloroacetate**2a**to phenol and chloroacetic acid.

4. Conclusion

p-Toluenesulfonicacid a biodegradable white solid, was used in the Fries rearrangement ofphenyl chloroacetate to2-chloro-1-(2-hydroxyphenyl)ethanone with very good conversion of around 70% and very good yield of the ortho product. To obtain suchperformances, a molar ratio of *p*-toluenesulfonic acid is not necessary. Hydroxyketones wereeasily separated from the aqueous solution by extraction with organic solvents. *P*-Toluenesulfonic acid, a biodegradable and easy to handle. It performances are similartoaluminium chloride (yield, conversion, selectivity) and has lower impact on the environment.

5. References

1. F. J. Waller, R. W. Van Scoyoc, *Chem. Tech.*,**1987**, *17*, 438.
2. B.B. Ramesh, IN **1993**,171,970 ShasunChemicals(m) Ltd., India
3. M.B. Hocking, J.Chem.Technol.Biotechnol.**1980**, 30,626.
4. Alessandro Bango, Willi Kantlehner, Ralf Kreb and GiacomboSaielli Z. Naturforsch 59b 2004 386
5. H. Shargi, E. Eshghi, Bull. Chem. Soc. Jpn. **66**, 135(1993).
6. Annie Commarieu, Wolfgang Hoelderich, Jean Alex Lalfitte, Marie-Pierre Dypont. J. Mol. Catalyst A: Chemical 2002, 137.
7. C. Venkatachalapathy, K. Pitchumani, Tetrahedron **53**,17171 (1997).
8. S. Kobayashi, M. Moriwaki, I. Hachiya, TetrahedronLett. **37**, 2053 (1996).
9. S. Kobayashi, M. Moriwaki, I. Hachiya, J. Chem. Soc.,Chem. Commun. 1527 (1995).
10. HosseinEshghi, Mohammad Rafie, Zinat Gordi and MoosaBohloli. J. Chem. Research (S) 2003, 763
11. N. N. Mamatkuukurov, A. K. Abdushukurov, Sh. Khidirov and S. Rakhmonova. Russian J. Orga. Chem. 2001 11 1668.
12. Satya Paul, Monoka Gupta. Synthesis 2004 11, 1789.