

One-step preparation of α -chlorostyrenes

Hanumant B. Borate,^{a,*} Abaji G. Gaikwad,^{b,*} Suleman R. Maujan,^a
Sangmeshwer P. Sawargave^a and Kamalakar M. Kalal^a

^a*Division of Organic Chemistry: Technology, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India*

^b*Chemical Engineering and Process Development Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India*

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Abstract— α -Chlorostyrenes were prepared via a one-step method involving Friedel–Crafts reaction of various aromatic substrates with acid chlorides in the presence of a heterogeneous Si–Fe catalyst.

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α -Chlorostyrenes are used as intermediates in the preparation of α -halomethyl ketones,¹ 1-diarylphosphino-2-arylethylenes,² 2-arylallyltitanocenes,³ α -thiocyanato-stilbenes,⁴ arylacetylenes,⁵ etc. They can be prepared by reaction of aryl alkyl ketones with PCl_5 followed by distillation,⁶ pyrolysis of a mixture of dihaloethylene and alkanes,⁷ Wittig reaction of ketones with $\text{Ph}_3\text{P}=\text{CHCl}$ ⁸ or addition of HCl to acetylenes in the presence of zinc chloride,⁸ reaction of diethyl chlorobenzylphosphonate with ketones,⁹ heating aryltrichloromethanes with $\text{P}(\text{OMe})_3$ in CCl_4 to give the intermediate aryl-dichloroethane and further conversion to α -chlorostyrenes,¹⁰ reaction of benzeneselenenyl chloride with olefins in the presence of aluminium chloride,¹¹ reaction of phenylselenium trichloride with olefins followed by selenoxide elimination,¹² reaction of acid chlorides with aromatic substrates in the presence of acid-treated Montmorillonite– FeCl_3 catalyst,¹³ halogenation of acetophenones with acid halides in the presence of Lewis acid,¹⁴ etc. These methods suffer from the disadvantages such as heating at high temperatures,⁷ costly or rare reagents,^{9–12} and low yields.¹³

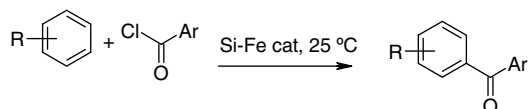
As a part of our ongoing efforts to explore the utility of heterogeneous catalysts for various organic reactions,^{15–18} we have studied various heterogeneous catalysts for applications in organic chemistry. Hetero-

geneous catalysts offer a number of advantages over homogeneous catalysts such as ease of work-up, recyclability of catalyst, and effluent treatment. During the course of our studies, we found that a heterogeneous Si–Fe catalyst catalyzed the Friedel–Crafts acylation of aromatic compounds.¹⁹ α -Chlorostyrenes were obtained in one-step as the major product in the case of acid chlorides having α -methylene groups. Our results are reported herein.

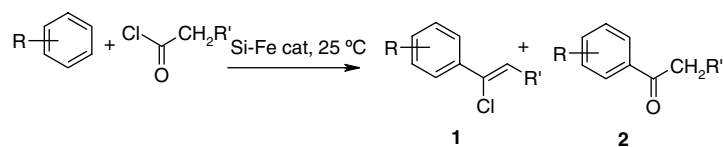
Initially anisole was reacted with benzoyl chloride in the presence of various catalysts. The Si–Fe catalyst,^{19,20} prepared from sodium trisilicate and ferric nitrate in the presence of ammonia and ammonium carbonate, afforded the corresponding Friedel–Crafts acylation product in 70% isolated yield on stirring the neat reaction mixture at rt (Table 1, entry 1). The reactions of various acid chlorides with anisole and thiophene resulted in the formation of acylated products²¹ (Table 1) in 70–77% yields. When anisole was reacted with propionyl chloride, a mixture of two products was obtained which was easily separated by column chromatography.²² The slower moving product obtained in 28% yield was found to be the Friedel–Crafts acylation product while the faster moving product, isolated in 65% yield, turned out to be the corresponding α -chlorostyrene.⁸ (Table 2, entry 1). A literature survey revealed that α -chlorostyrenes were obtained as side products in Friedel–Crafts acylations using acid-treated Montmorillonite– FeCl_3 catalyst¹³ in 1–9% yields. The higher yield obtained in our reaction prompted us to develop this method for the one-step preparation of α -chlorostyrenes. Accordingly, reactions of various aliphatic acid

Keywords: α -Chlorostyrenes; Friedel–Crafts acylation; Heterogeneous catalysts; Acid chlorides.

* Corresponding authors. Fax: +91 2025902629 (H.B.B.); e-mail: hb.borate@ncl.res.in


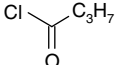
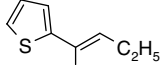
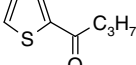

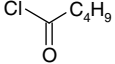
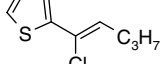
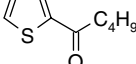

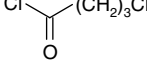
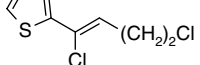
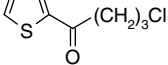
Table 1. Friedel–Crafts acylation with aromatic acid chlorides

Entry	Substrate	Acid chloride	Product (% yield)
1			(70)
2			(76)
3			(75)
4			(79)
5			(77)

Table 2. Preparation of α -chlorostyrenes

Entry	Substrate	Acid chloride	Product 1 (% yield)	Product 2 (% yield)
1			(65)	(28)
2			(67)	(25)
3			(43)	(49)
4			(41)	(48)
5			(60)	(30)
6			(36)	(40)
7			(57)	(32)
8			(46)	(28)

Table 2 (continued)

Entry	Substrate	Acid chloride	Product 1 (% yield)	Product 2 (% yield)
9			 (26)	 (66)
10			 (17) ^a	 (73)
11			 (19) ^a	 (68)

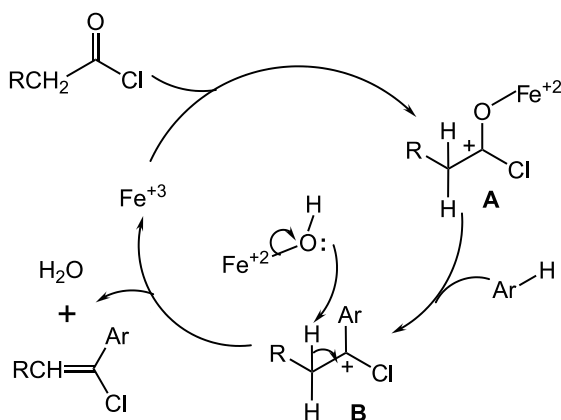
^aThe reactions had to be worked-up in 10 min in order to isolate the α -chlorostyrenes.

chlorides with aromatic substrates were carried out to afford the corresponding α -chlorostyrenes in good yields. Comparison of ^1H NMR data of the faster moving products obtained in the reactions of anisole and toluene with propionyl chloride (Table 2, entries 1 and 5) showed that the products were (Z)-1-chloro-1-(4-methoxyphenyl)-1-propene and (Z)-1-chloro-1-(4-methylphenyl)-1-propene, respectively.⁸

The α -chlorostyrenes were easily separated from the corresponding Friedel–Crafts acylation products by column chromatography. These compounds had variable stability ranging from 1–2 days to 1–2 weeks after which they either decomposed or were converted into the corresponding Friedel–Crafts acylation products.

Clark et al. have proposed a mechanism for the formation of α -chlorostyrenes from aromatic substrates¹³ involving a chlorovinyl cation or chlorohydroxy cation. We envisage that the Fe^{3+} present in Si–Fe catalyst helps the formation of cation **A** from the acid chloride, which on reaction with the substrate leads to the formation of cation **B** and a Fe^{2+} species. Cation **B** is transformed to the α -chlorostyrene and Fe^{3+} is regenerated (Scheme 1).

In conclusion, α -chlorostyrenes were prepared by a one-step method from aromatics and acid chlorides using a heterogeneous, Si–Fe catalyst at room temperature with or without solvent.



Scheme 1.

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20. To a solution of sodium trisilicate (24.21 g, 0.3 mol) in water (250 ml), a solution of ferric nitrate (40.4 g, 0.1 mol) in water (75 ml) and a solution of ammonium carbonate containing ammonia [ammonium carbonate (2.34 g, 0.05 mol), 25% ammonia solution (34 ml, 0.5 mol) diluted to 75 ml] were added simultaneously at room temperature with stirring. The solid mass formed in the aqueous solution was stirred for 12 h, filtered, dried at 120 °C for 12 h, calcined at 500 °C for 3 h, powdered and used for reactions. This iron silicate type catalyst had an acidity of 0.4 mmol/g (by the ammonia method), surface area 271 m²/g (by BET method) and atomic weight ratio C = 4.14%, O = 64.6%, Si = 18.11% and Fe = 13.15% (by EDAX).
21. All the products showed satisfactory spectral data.
22. Typical experimental procedure: To a two-neck flask equipped with a guard tube (CaCl₂), activated (150 °C, 2 h) catalyst (10% by weight, 20 mg) was added. To this was added anisole (0.2 ml, 1.85 mmol) followed by the addition of propionyl chloride (0.16 ml, 1.85 mmol). The reaction mixture was allowed to stir at 25 °C for 10 h. The reaction mixture was then filtered to remove the catalyst and washed with ethyl acetate (2 × 3 ml). The filtrate and washings were combined, washed with water, dried over sodium sulfate and concentrated to give a crude product. Purification by column chromatography over silica gel afforded (*Z*)-1-chloro-1-(4-methoxyphenyl)-1-propene⁸ (220 mg, 65%) as the faster moving spot. ¹H NMR (CDCl₃, 200 MHz): δ 1.94 (d, *J* = 8 Hz, 3H), 3.83 (s, 3H), 6.09 (q, *J* = 8 Hz, 1H), 6.88 (d, *J* = 10 Hz, 2H), 7.50 (d, *J* = 10 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃+CCl₄): δ 15.11, 55.22, 113.57 (2C), 120.38, 127.60 (2C), 131.21, 133.66, 160.63; GC-MS: *m/z* 184 (26%, M⁺) and 182 (79, M⁺), 147 (100), 131 (20), 115 (45), 103 (32), 91 (54), 77 (40). Anal. Calcd for C₁₀H₁₁ClO: C, 65.75; H, 6.03; Cl, 19.45. Found: C, 65.58; H, 5.91; Cl, 19.64.
- Further elution afforded 1-(4-methoxyphenyl)-propan-1-one (85 mg, 28%) as a thick liquid. ¹H NMR (CDCl₃, 200 MHz): δ 1.21 (t, *J* = 8 Hz, 3H), 2.96 (q, *J* = 8 Hz, 2H), 3.87 (s, 3H), 6.93 (d, *J* = 10 Hz, 2H), 7.95 (d, *J* = 10 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃): δ 8.36, 31.33, 55.36, 113.58 (2C), 129.92, 130.13 (2C), 163.21, 199.43; GC-MS: *m/z* 164 (11%, M⁺), 135 (100), 107 (16), 92 (19), 77 (30). Anal. Calcd for C₁₀H₁₂O₂: C, 73.17; H, 7.32. Found: C, 72.87; H, 7.42.