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Research Note

Synthesis of (Z)-β-bromostyrenes from cinnamic acid derivatives through debrominative decarboxylation of dibromoaryl propanoic acids using KF/Al_2O_3

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KEYWORDS
(Z)-β-Bromostyrene; KF/Al_2O_3; Debrominative decarboxylation; *Anti*-2,3-dibromo-3-aryl propanoic acid.

Abstract. An efficient method for the stereoselective synthesis of (Z)-1-bromo-1-alkenes through debrominative decarboxylation of *anti*-2,3-dibromoalkanoic acids using KF/Al_2O_3 is described. KF/Al_2O_3 showed to be an effective base in this reaction leading to a relatively high selectivity and good to excellent yield of the (Z)-1-bromo-1-alkenes.

1. Introduction

1-Halo-1-alkenes are important precursors in many useful organic transformations including Stille, Suzuki, Sonogashira and Buchwald-Hartwig reactions [1]. Geometrically pure alkenyl halides have gained increasingly interest as they are required in the stereospecific synthesis of conjugated polyenes and eneyens [2]. Many biologically active natural products possess (Z)-olefin moiety in their structures (e.g., rhodopsins [3], eicosanoids [4] and enediyne antibiotics [5]).

Numerous methods are reported for the preparation of (E)-1-bromo-1-alkenes. Among the reported methods, the Hunsdiecker reaction is a popular approach, which involves the oxidative bromodecarboxylation of a silver salt of carboxylic acid with bromine. This reaction requires a heavy metal salt, and high temperature. Several attempts were made to improve this reaction using various reagents [6]. In the other hand, there are a few methods for the stereo-controlled preparation of (Z)-1-halo-1-alkenes including: replacement of the boronic acid substituent by bromine in alkenyl boronic acids [7], haloalkenylation of aldehydes with Wittig type reagents [8], Pd-catalyzed reaction of 1,1-dibromo-1-alkenes by tributyltin hydride [9], hydroalumination of alkynes [10], hydroboration of 1-halo-1-alkynes followed by protonolysis [11] and debrominative decarboxylation of cinnamic dibromides [12]. Although many of these methods are effective, some of these synthetic methods have several drawbacks, including the use of complex reagents, long reaction times, low yields or need to expensive instruments such as microwave. Among these procedures, debrominative decarboxylation of 2,3-dibromoalkanoic acids is a synthetically useful route for the preparation of (Z)-vinyl bromides. Several improvements of this method were reported with a number of solvents and bases [12]. Some bases, such as Cs_2CO_3 are very moisture sensitive which reduce its ability in many organic reactions, or organic bases like NEt_3 are not easily separated from the reaction mixture. On the other hand, application of KF/Al_2O_3 in organic synthesis has provided new methods for a wide range of organic reactions. It has

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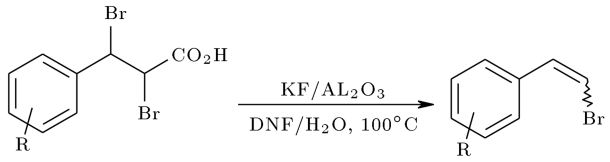
Table 1. Effect of different solvents on the yield of **2**.

Entry	Solvent	Yield[a] (%)	Entry	Solvent	Yield (%)
1	H_2O	10	8	THF:H_2O (2:1)	60
2	$PhCH_3$	20	9	DMF:H_2O (2:1)	93
3	CH_2Cl_2	20	10	DMF:H_2O (1:1)	96
4	THF	25	11	DMF:H_2O (1:2)	80
5	DMF	55	12	DMF:H_2O (4:1)	75
6	$PhCH_3$:H_2O (2:1)	65	13	DMF:H_2O (1:1)	90[b]
7	CH_2Cl_2:H_2O (2:1)	55	14	DMF:H_2O (1:1)	70[c]

[a]: Reaction conditions: substrate **1** (1 mmol), KF/Al_2O_3 (1 mmol), time (1.15 h), temperature (100°C), solvent (6 mL).

[b]: Substrate **1** (1 mmol), KF/Al_2O_3 (2 mmol).

[c]: Substrate **1** (2 mmol), KF/Al_2O_3 (1 mmol).



R= Electron donating and electron withdrawing groups

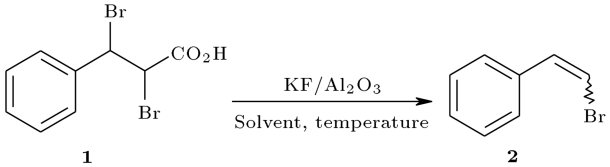
Scheme 1. Preparation of (*Z*)-*β*-bromostyrenes from 2,3-dibromopropanoic acids in the presence of KF/Al_2O_3.

strong basic character and has been used in a number of reactions. In many cases, the use of this base provides milder conditions and simpler procedures than previously reported methods [13].

Recently, we have used KF/Al_2O_3 as a suitable base in many cross-coupling reactions [14]. Herein, we report a convenient method for the synthesis of (*Z*)-*β*-bromostyrenes from cinnamic acid derivatives through debrominative decarboxylation of dibromoaryl propanoic acids using KF/Al_2O_3 as a cheap, nontoxic and stable base which can be easily separated at the end of the reaction (Scheme 1).

2. Results and discussion

To find the optimum reaction conditions, the reaction of *anti*-2,3-dibromo-3-phenyl propanoic acid with KF/Al_2O_3 was chosen as a model reaction (Scheme 2), and the progress of reaction and the *Z*/*E* ratio of the corresponding products were determined by GC analysis.

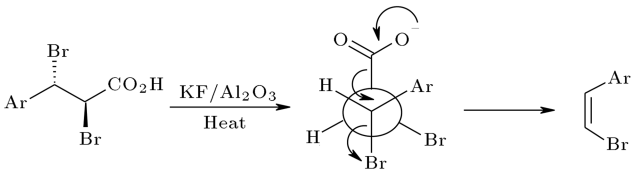


Scheme 2. Transformation of 2,3-dibromopropanoic acids to (*Z*)-*β*-bromostyrenes in different conditions.

Various conditions were examined to optimize the yield and the stereoselectivity of this reaction and the results are shown in Table 1. As is clear from Table 1, water or organic solvents alone gave a low yield of the products (entries 1-5), whereas when the reaction was conducted in the mixture of water and organic solvents, the reaction yields were increased (entries 6-14). However, the best reaction conditions were ascertained by treatment of 1 equivalent of *anti*-2,3-dibromo-3-phenyl propianoic acid with 1 equivalent of KF/Al_2O_3 in 6 ml DMF:H_2O (2:1) at 100°C, giving excellent yield of the corresponding (*Z*)-1-bromo-1-alkenes (**2**) with high (*Z*)-selectivity (entry 9).

In order to examine the applicability and limitations of the above protocol, a series of dibromo aryl propanoic acid derivatives with electron donating and electron withdrawing groups were treated with KF/Al_2O_3 under optimum conditions, and, as shown in Table 2, a good to excellent yield of the corresponding (*Z*)-*β*-bromostyrenes was obtained.

When unsubstituted cinnamic acid dibromides (Table 2, entries 1, 12 and 13) and those derivatives with electron-withdrawing groups (Table 2, entries 2-7 and 11) were used, the reactions proceeded via E_2-like mechanism involving simultaneous loss of carbon dioxide and bromide ion, as reported in the literature [12g], to give the corresponding (*Z*)-*β*-bromostyrenes in excellent yields with high stereoselectivies (Scheme 3). In the case of weak electron donating group such as methyl group (Table 2, entry 8) the reaction proceeded well to give the desired product in excellent yield but the



Scheme 3. Stereospecific transformation of *anti*-2,3-dibromopropanoic acids to (*Z*)-*β*-bromostyrenes.

Table 2. Stereoselective synthesis of (Z)-β-bromostyrenes from corresponding cinnamic acid dibromides.

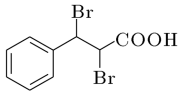
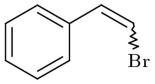
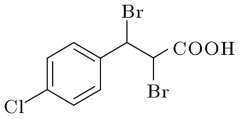
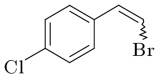
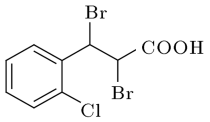
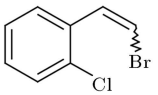
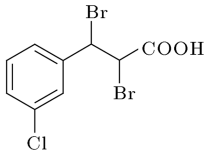
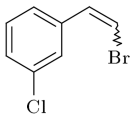
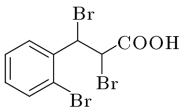
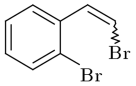
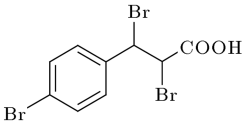
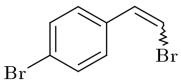
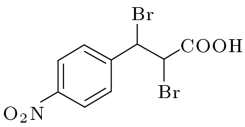
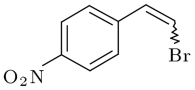
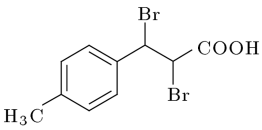
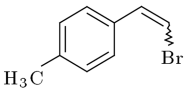
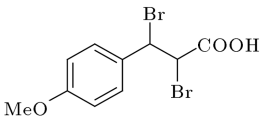
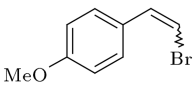
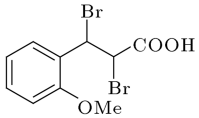
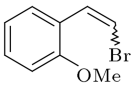
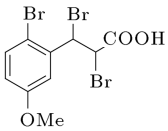
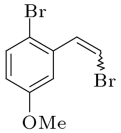
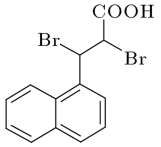
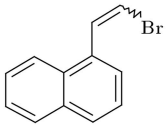
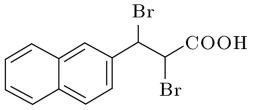
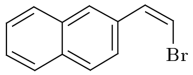
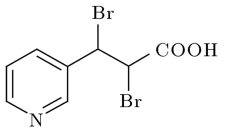
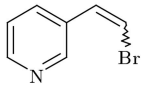
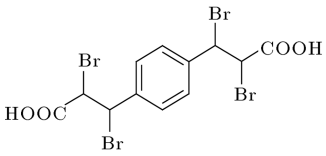
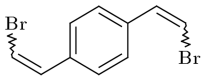
Entry	Substrate	Product	Yield (%)[a,b]	Z/E[c]
1			95	95/5
2			95	98/2
3			75	98/2
4			85	99/1
5			90	99/1
6			90	92/8
7			97	99/1
8			95	86/14
9			90	18/82
10			90	10/90
11			90	95/5
12			95	91/9

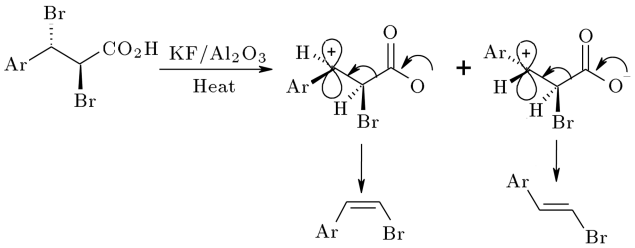
Table 2. Stereoselective synthesis of (Z)-β-bromostyrenes from corresponding cinnamic acid dibromides (Continued).

Entry	Substrate	Product	Yield (%)[a,b]	Z/E[c]
13			95	89/11
14			60	97/3
15			85	96/4

[a]: Yields refer to isolated products.

[b]: All products were identified by comparing ^{1}H and ^{13}C NMR spectra with those of authentic samples reported in literature.

[c]: The Z/E ratios were determined by GC and ^{1}H NMR analysis.



Scheme 4. Stereospecific transformation of *anti*-2,3-dibromopropanoic acids bearing strong electron-donating groups to (E)-β-bromostyrenes.

stereoselectivity of Z/E was decreased a little (86/14). Interestingly, stronger electron-donating group like methoxy at ortho and para positions of cinnamic acid dibromide showed opposite Z/E stereoselectivity (Table 2, entries 9-10). This might be due to the elimination of bromide ion and CO_2 through E_1-like pathway. Probably, elimination occurs predominately through the more stable conformation of the intermediate carbocation to afford the (Z)-and (E)-vinyl bromides, with a preferential formation of (E)-isomer (Scheme 4). Anti-3-pyridyl-2,3-dibromopropionic acid under optimum reaction conditions showed the expected Z/E stereoselectivity (97/3), although the yield was moderate (entry 14). Finally, (Z)-1,4-bis-(β-bromovinyl)benzene was obtained in high yield under reaction conditions with excellent Z/E stereoselectivity (entry 15).

3. Conclusion

In conclusion, we have developed an efficient method for stereoselective synthesis of (Z)-β-arylvinylbromides from the corresponding *anti*-3-aryl-2,3-dibromopropanoic acids using KF/Al_2O_3 as base in DMF/H_2O solvent. In the case of strong donating group such as methoxy, (E)-β-arylvinylbromides were obtained in high yields. Products in all reactions were easily separated from the reaction mixture and the stereoselectivity of the products were determined by ^{1}H NMR spectroscopy.

4. Experimental

4.1. General information

Anti-2,3-dibromoalkanoic acids (**1**) were obtained by bromination of the corresponding *trans*-α,β-unsaturated carboxylic acids according to the procedure reported in the literature [12g]. All the products were characterized by ^{1}H and ^{13}C NMR data and GC analyses. ^{1}H and ^{13}C-NMR spectra were obtained on a Bruker Avance instrument at 400 and 100 MHz, respectively using $CDCl_3$ as solvent. GC analyses were performed on a Perkin Elmer 8500 instrument using a Capillary column 30 M with a FID detector under helium as carrier gas.

4.2. General procedure for stereoselective synthesis of (Z)-β-bromostyrenes from anti-2,3-dibromoalkanoic acids

Into a round bottom flask, equipped with a magnetic stirrer and a condenser, *anti*-3-aryl-2,3-dibrobopropanoic acids (1 mmol), KF/Al_2O_3 (1 mmol) and DMF:H_2O (2:1, 6 mL) was added. Then the mixture was stirred for 1.15 h at 100°C. After completion of the reaction, as indicated by the TLC, the cooled mixture was extracted with diethyl ether (20 mL) and the combined organic layers were washed with water and brine, dried with anhydrous $MgSO_4$ and filtered. Evap-

oration of the solvent under reduced pressure gave almost pure products. If further purification was needed, the crude products were purified by column chromatography on silica gel with ethylacetate-hexane (1:4) as eluent. Stereoselectivity and characterization of the products were determined by ^{1}HNMR and ^{13}C NMR spectroscopy and compared with authentic samples.

4.3. Spectral data of products in Table 2

(Z)-β-Bromostyrene (entry 1): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.47 (d, J = 8.2 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H), 7.34-7.45 (m, 3H), 7.72-7.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.33, 105.40, 128.89, 132.14, 138.26. Z/E = 95/5.

(Z)-β-Bromo-4-chlorostyrene (entry 2): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.48 (d, J = 8.2 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 107.19, 128.48, 130.27, 131.24, 133.35, 134.06. Z/E = 98/2.

(Z)-β-Bromo-2-chlorostyrene (entry 3): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.62 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.31-7.34 (m, 2H), 7.43-7.45 (m, 1H), 7.85-7.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 109.43, 126.29, 129.44, 129.47, 129.99, 130.32, 133.33, 133.55. Z/E = 98/2.

(Z)-β-Bromo-3-chlorostyrene (entry 4): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.52 (d, J = 8.2 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 7.32-7.34 (m, 2H), 7.56-7.59 (m, 1H), 7.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 108.02, 127.15, 128.36, 128.87, 129.52, 131.17, 134.15, 136.62. Z/E = 99/1.

(Z)-β-Bromo-2-bromostyrene (entry 5): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.61 (d, J = 8.4 Hz, 1H), 7.20-7.25 (m, 2H), 7.35-7.39 (m, 1H), 7.63 (dd, J = 8.0, 1.2 Hz, 1H), 7.81 (dd, J = 8.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 109.40, 123.76, 126.93, 129.65, 130.55, 132.36, 132.68, 135.16. Z/E = 99/1.

(Z)-β-Bromo-4-bromostyrene (entry 6): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.49 (d, J = 8.2 Hz, 1H), 7.03 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 107.33, 122.30, 130.51, 131.29, 131.43, 133.78. Z/E = 92/8.

(Z)-β-Bromo-4-nitrostyrene (entry 7): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.70 (d, J = 8.4 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.8 Hz, 2H), 8.26 (d, J = 8.8 Hz, 2H). Z/E = 99/1.

(Z)-β-Bromo-4-methylstyrene (entry 8): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.37 (s, 3H), 6.40 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 8.0 HZ, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.44, 105.50, 126.10, 128.99, 129.53, 132.24, 138.36. Z/E = 86/14.

(E)-β-Bromo-4-methoxystyrene (entry 9): ^{1}H NMR (400 MHz, $CDCl_3$) (E): δ (ppm) = 3.83 (s, 3H), 6.63 (d, J = 13.8 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 13.8 Hz, 1H), 7.26 (d, J = 8.8 Hz, 2H); ^{1}H NMR (400 MHz, $CDCl_3$) (Z): δ (ppm) = 3.83 (s, 3H), 6.32 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (E): δ (ppm) = 55.32, 104.00, 113.60, 114.19, 127.36, 128.77, 136.55. Z/E = 18/82.

(E)-β-Bromo-2-methoxystyrene (entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) (E): δ (ppm) = 3.86 (s, 3H), 6.88-6.94 (m, 3H), 7.25-7.29 (m, 2H), 7.32 (d, J = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (E): δ (ppm) = 55.39, 107.87, 110.95, 120.71, 124.72, 127.95, 129.28, 133.03, 156.56. Z/E = 10/90.

(Z)-β-Bromo-2-bromo-5-methoxystyrene (entry 11): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.84 (s, 3H), 6.60 (d, J = 8.2 Hz, 1H), 6.79 (dd, J = 8.8, 3.2 Hz, 1H), 7.20 (d, J = 8.2 Hz, 1H), 7.40 (d, J = 2.8 Hz, 1H), 7,49 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.59, 109.35, 115.68, 114.24, 115.89, 132.24, 133.19, 135.67, 158.33. Z/E = 95/5.

(Z)-1-(β-Bromovinyl)naphthalene (entry 12): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.79 (d, J = 8.0 Hz, 1H), 7.53-7.60 (m, 3H), 7.63 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.2 Hz, 1H), 7.88-7.98 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 110.11, 124.25, 125.23, 126.04, 126.32, 126.86, 128.58, 128.64, 131.15, 131.47, 132.25, 133.55. Z/E = 91/9.

(Z)-2-(β-Bromovinyl)naphthalene (entry 13): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.54 (d, J = 8.2 Hz, 1H), 7.26 (d, J = 8.2 Hz, 1H), 7.49-7.53 (m, 2H), 7.82-7.90 (m, 4H), 8.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) =106.71, 126.31, 126.37, 126.45, 126.51, 127.67, 127.75, 128.31, 128.60, 132.42, 133.01, 133.06. Z/E = 89/11.

(Z)-3-(β-Bromovinyl)pyridine (entry 14): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.55 (d, J = 8.2 Hz, 1H), 7.02 (d, J = 8.2 Hz, 1H), 7.28 (dd, J = 8.0, 4.4 Hz, 1H), 8.11 (tt, J = 8.0, 3.6 Hz, 1H), 8.05 (dd, J = 4.8, 1.6 Hz, 1H), 8.74 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) =109.29, 123.11, 129.09, 130.10, 135.60, 148.93, 150.14. Z/E = 97/3.

(Z)-1,4-bis-(β-Bromovinyl)benzene (entry 15): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.49 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 7.73 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 106.94, 128.85, 131.88, 134.82. Z/E = 96/4.

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