Electrophilic Diamination of Functionalized Alkenes Directly without Any metal Catalysts

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Research Article

Abstract: A novel direct electrophilic diamination reaction of α, β-unsaturated esters has been established without the use of any metal catalysts resulting in the synthesis of α, β differentiated diamines and imidazolines. Different aromatic and aliphatic ester had been synthesize and reactions employ electron-deficient alkenes as the substrates and take the advantage of readily available N,N-dibromo-p-toluene sulfonamide ($TsNBr_2$) as electrophilic nitrogen source and acetonitrile as the nucleophilic nitrogen source. A new mechanism has also been proposed to explain the resulting regio – and stereo selectivity.

Keywords: α, β- unsaturated esters, Bromanine – T, Acetonitrile, Electrophilic diamination.

Introduction

In organic chemistry formation of regio – and stereoselective diamination of alkenes has been a challenging and important topic because the resulting vicinal diamine products are extremely important for medicinal chemistry and pharmaceutical research.[1,2] Enatiomerically pure diamine derivatives are often utilized as chiral auxillaries and ligands for asymmetric synthesis and catalysis.[3-6] so far, most olefinic diamination have been achieved by using non functionalized alkenes as the starting materials in the presence of various metal promoters derived from metals such as thallium. Palladium, osmium, and mercury.[7.8] This article describes the synthesis of aromatic and aliphatic α, β –unsaturated esters which employs as electron-deficient alkenes substrates and take the advantage of readily available N,N–Dibromo-p-toluene sulfonamide ($TsNBr_2$) as electrophilic nitrogen source and acetonitrile as the nucleophilic nitrogen source resulting in α, β differentiated diamines and imidazolines. It is very convenient to carry out the present diamination reaction simply by mixing reactants in a one pot operation at room temperature. Since there are no sensitive catalysts involved, the reaction can thus be performed without the special protection from insert gases.

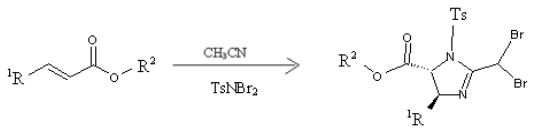
Results and Discussion

The synthesis of α, β differentiated diamines and imidazolines are carried out by direct electorphilic diamination reaction of α ,β- unsaturated esters without the use of any metal catalysts. The reactions between electron-deficient alkenes, N,N-Dibromo-p-toluene sulfonamide ($TsNBr_2$) and acetonitrile result in different aliphatic and aromatic esters for which new mechanism has also been proposed to explain the resulting region – and stereoselectivity . The melting point, synthesis time in hour, Stereo selectivity, and percent yield of the synthesize products are stated in Table no.1.the further characterization and qualitative analysis was done on the synthesized products by using FTIR, H^1-NMR,C_{13} MR. This confirmsthe authentification of the synthesized product.

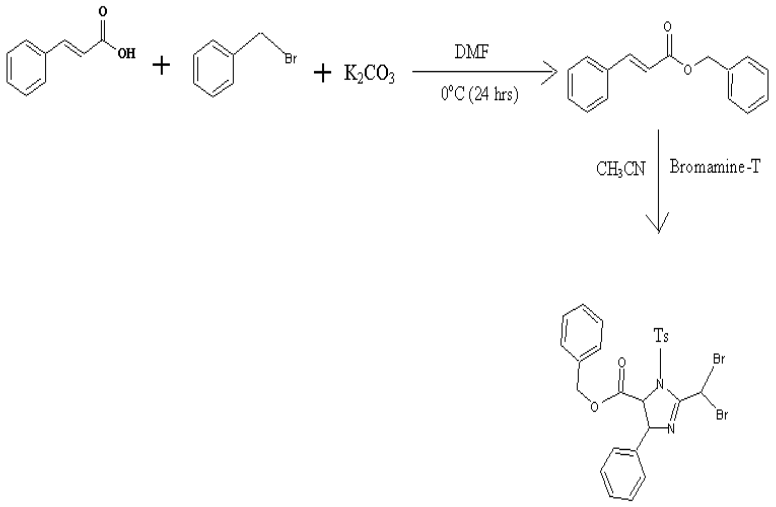
Experimental Procedures

Different α, β- unsaturated esters required for the reaction are synthesized by continuous stirring of cinnamic acid with different bromide reagents like benzyl bromide, methyl bromide, ethyl bromide and propyl bromide in the presence of K_2CO_3 and DMF (dimethylformamide) at 0^0C for 24 hours.

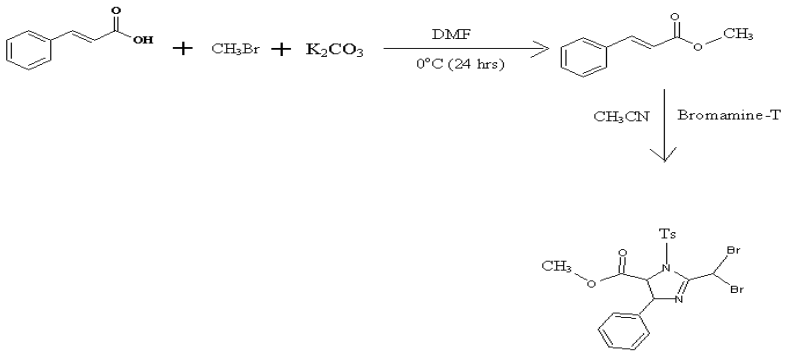
The corresponding esters formed are recrystalized and purified esters are subjected to further direct diamination reactions in which esters and N, N-dibromo-p-toluene sulfonamide ($TsNBr_2$) are taken into a dry vial. Freshly distilled acetonitrile was then added into the above mixture. The resulting solution was stirred at room temperature until the reaction was finished as revealed by TLC. The reaction times are indicated in Tables 1. The reaction was quenched by 5.0 ml of saturated aqueous Na_2So_3 solution. The other solid precipitates in the reaction was filtered off and washed with EtOAc through 4 A^O (angstron) molecular sieves. The two phases were separated from the filtrate and the aqueous phase was extracted further with EtOAc. The combined organic phase was washed with brine and dried with anhydrous sodium sulfate. Purification by flash chromatography provided pure product.



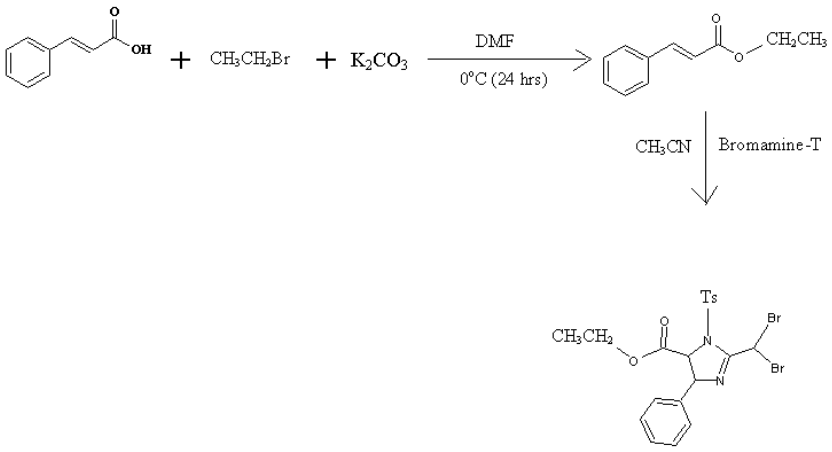
Scheme I



Scheme II



Scheme III



Scheme IV

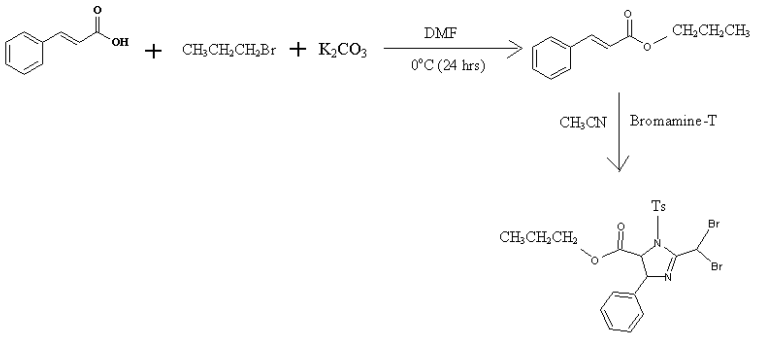
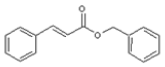
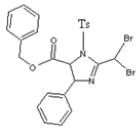
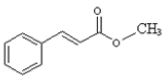
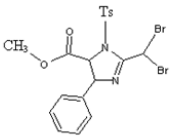
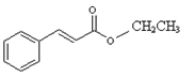
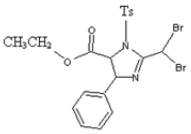
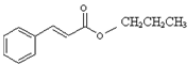
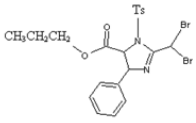


Table 1: Results of Non Catalytic Diamination of α, β- unsaturated esters

Sr. No.	Substrates	Products (±)	Stereoselectivity	Time (h)	yield (%)
1			>95	35	73
2			>95	32	68
3			>95	31	70
4			>95	34	72

Scheme I

I.R. 3057 (w), 2924 (m) 1759 (s)
1641 (m) 1454 (m) 1370 (s)
1160 (s) 1090 (m) 10181 (w) 728 (w)
666 (s)

H1 NMR 400 MHz
7.67 (2H, d, J= 8Hz), 7.26 – 7.15 (5H, M),
7.09 (1H, s), 6.87 (24, d, J = 8Hz) s 21 (1H, d, J = MHz)
5.56 (1H, d, J = MHz), 3.81 (3H, S) 2.40 (3H, s)

C^{13} (100 MHz)
169.7, 156.9, 145.6, 134.4, 133.6, 130.0,
286.6, 127.8, 127.5, 125.7, 71.7, 69.4, 53.1, 27.7, 21.5

Scheme II

IR = 2921 (M) 2852 (W), 1745 (S) 1640 (W)
1371 (W) 1162 (S) 1067 (M) 1019 (M)
608 (M) 667 (S)

H^1 NMR (300 MHz CDCl3)

7.65 (2H, d, J = 6Hz), 7.63 – 7.32 (5H,m)
7.25 – 7.12 (5H, m) 7.076 1H, s) 6.81 (2H, d, J= 6Hz)
5.23 (2H, s) 5.18 (1H,d, J=3Hz) 4.60 (1H, d, J = 3Hz)
2.39 (3H, s)

C13 (75 MHz, $CDCI_3$)
169.1, 157.0, 145.6, 139.3, 130.0, 128.7
128.6, 128.2, 127.9, 127.6, 125.8, 71.88, 69.61, 67.7, 24.6, 27.7, 21.6.

Scheme III
I.R. 2919(W) 710 (S) 1574 (M) 421 (W)
1258 (W) 1036 (S) 1000(M) 701 (M)

H1 NMR (400MHz, $CDCl_3$)
7.68 (2H, d, J = 8Hz) 7.26 – 7.15 (5H, m)
7.09 (1H, s), 6.88 (2H, d, J= 8Hz)

5.19 (1H, d, 4H2) 4.54 (1H, d, J = 4H2)
2.26(2H, 9, J = 8Hs) 2.40 (3H,S)
1.30 (3H, t, J = 8Hz)

C13 (100 MHz) CDCl3)
169.3, 157.0, 145.6, 139.5, 153.9, 130.0, 128.7, 128.1, 127.9, 127.6, 125.8, 71.9, 69.6, 62.3, 27.9, 21.6, 14.0

Scheme IV
Hl (300MHz, CDC13)
7.79(2H,d,J= 9Hz),7.71(2H,D,J = 9Hz)
7.44(2H,d,J = 6Hz), 7.34-7.23(6H,M)
7.08 (1H,s),6.87 (2H,d,J=6Hz)4.47 (1H,d,J=6Hz)
5.01 (1H,d,J=6Hz) ,2.46 (3H, S)

C13 (75MHz, CDC13)
192.5, 157.1, 145.8, 141.0, 138.7, 134.2, 131.8
130.2, 129.3, 129.1, 128.7, 127.9, 120.5, 72.3,
72.0, 27.5, 21.7

Conclusion

A novel direct electrophilic diamination reaction of α, β-unsaturated esters has been successfully carried out without the use of any metal catalysts resulting in the synthesis of α, β differentiated diamines and imidazolines. The products firm are aromatic and aliphatic ester by reaction election-deficient alkenes with N,N-Dibromo –p-toluene sulfonamide ($TsNBr_2$) in the presence of acetonitrile as the nucleophilic nitrogen source.

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