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FULL PAPER

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Olefination of *N*-Sulfinylimines under Mild Conditions

Shubhendu Dhara [a] and Charles E. Diesendruck*[a]

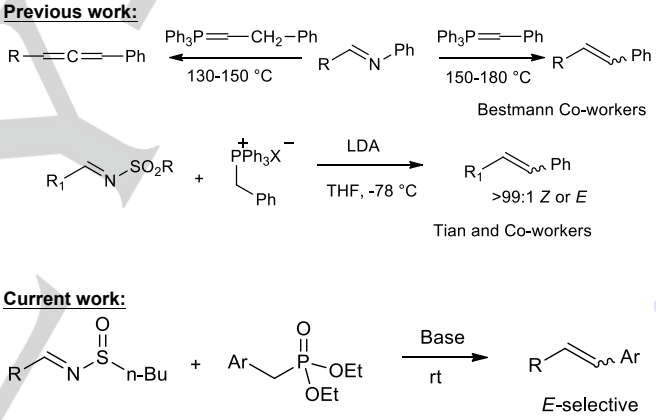
Abstract: A very simple and efficient diastereoselective synthesis of 1,2-disubstituted alkenes has been achieved under mild conditions. The sulfoxide stabilised *N*-sulfinylimine reacted with *in situ* generated phosphonate carbanion to give 1, 2-disubtituted alkenes in good to excellent yields. Different aryl phosphonate reacted with a range of electronically diverse *N*-sulfinylimine to afford in almost greater than 99:1 *E*-selective alkenes. The most important feature of this protocol is that the reaction can be performed at room temperature using inexpensive sodium hydride as the most effective base to generate the reactive phosphonate carbanion producing up to 85 % isolated *E*-selective alkenes.

Introduction

Olefins are the ubiquitous building blocks in many naturally occurring bioactive molecules and important reactive intermediates in numerous organic transformations.[1] A mammoth of organic reactions including nucleophilic additions to carbonyls (such as Wittig reaction,[2] Peterson olefination,[3] and Julia olefination),[4] additions to alkynes,[5] alkenylations,[6] eliminations,[7] alkyne reductions,[8] olefin metatheses[9] among others[10] have been effectively devised for the stereoselective synthesis of olefins. Importantly, new approaches for the synthesis of olefins are still being investigated, as transformation of different functional groups into olefins may be key in the total synthesis of natural compounds, drugs etc.

Electrophilic imines have been attracting much interest recently owing to their simple preparation and usefulness as directing group as well as inherent reactivity towards addition reactions in organic chemistry.[11] Particularly, *N*-protected imines including *N*-sulfinyl,[12] *N*-phosphonyl,[13] *N*-phosphoryl,[14] and *N*-phosphinyl[15] have been used as chiral auxiliaries in nucleophilic addition reactions. Given the importance of these electrophilic imines in stereoselective synthesis as chiral auxiliaries,[16] it is surprising that their reactions with phosphorous ylides have not been studied, as their transformation into new useful functional groups after exercising their role as directing group and/or chiral auxiliary.

The Wittig reaction with stabilized and semi-stabilised phosphoniumylides has been studied to a great extent and its use in the synthesis of olefins (with or without stereoselectivity) is massive.[17] In contrast, the reaction of imines with phosphonium ylides, while addressed, still requires further investigation and optimization. Bestmann *et al.* first addressed this reaction in 1963, but extremely high temperatures (in which imines are probably not stable) were required to induce any reactivity between imines and phosphonium ylides. Recently, Tian *et al.* reported the stereoselective olefination of *N*-sulfonyl imines with stabilised and unstabilised phosphonium ylides under mild conditions.[18] His results inspired us to further advance this reaction using the more useful, but less reactive, *N*-sulfinyl imines with Wittig-Horner-Emmons reagents. To the best for our knowledge, *N*-sulfinyl imines have not been tested as ractants in the Wittig reaction and the stereoselectivity of this reaction needs to be understood (Scheme 1), as the *N*-sulfinyl imines can be converted to olefins after their use as directing groups and/or chiral auxiliaries in different chemical reactions.



Scheme 1: Reaction of imines and phosphonium reagents

Results and Discussion

Initially, we tested the reaction between *N*-sulfinylimines with Wittig reagents, but to our surprise, while good yields were obtained under mild conditions, a ca. 1:1 mixture of *E/Z* isomers (Scheme 2) was obtained. To improve selectivity, we decided to test Wittig-Horner-Emmons stabilized carbanions, as these react slower and provide enough time to direct the reaction to thermodynamic product.[19] Indeed, when arylphosphonates were reacted with *N*-sulfinylimines, *E* olefins were obtained almost exclusively. These initial results first of all demonstrate the high reactivity of *N*-sulfinylimine compared to regular imines, as no heating is required. In addition, the high diastereoselectivity shows the usefulness of this reaction in converting these important directing groups and chiral auxiliaries into olefins, which can be further functionalized in a multi-step synthesis.

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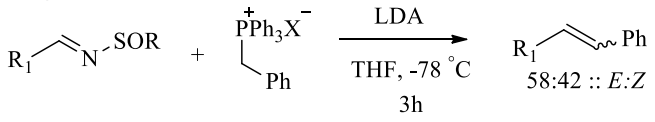
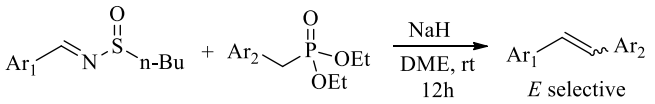
Wittig Reaction:

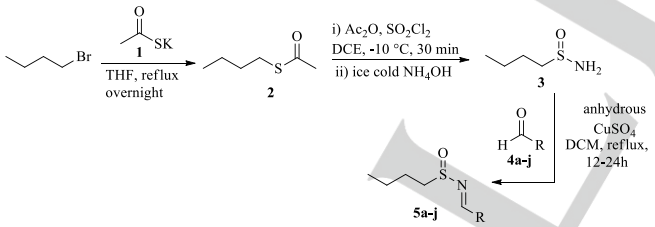


Wittig-Horner-Emmons:



Scheme 2: Reaction of *N*-sufinylimines with semistabilized triphenylphosphonium ylides and arylphosphonate carbanions

There are many approaches to the synthesis of *N*-sulfinylimines. For this research, we decided to prepare butane-1-sulfinamide **3** and directly condense it with different aldehydes. Importantly, **3** may be prepared and attached as a single enantiomer[13] serving as a chiral auxiliary; however, we decided to initially use the racemic mixture, as to test the diastereoselectivity without the advantage of the chiral auxiliary. Following a reported procedure (Scheme 3),[20] we reacted 1-bromobutane and potassium ethanethioate **1** in refluxing THF, producing S-butyl ethanethioate **2** quantitatively. Amidation of S-butyl ethanethioate to the corresponding S-butyl sulfinamide **3** was accomplished in two steps in one pot: first, oxidation of ethanethioate using acetic anhydride and sulfuryl chloride in 1,2-dichloroethane (DCE) at -10 ˚C and subsequently, converted to **3** by treatment with ice cold aqueous ammonium solution. For the preparation of *N*-sulfinylimines, various aldehydes (**4a-j**) were employed. The imines (**5a-j**) are formed with the help of the Lewis acidic dehydrated copper sulphate in refluxing DCM (table 1).



Scheme 3: Synthesis of butylsufinylimines

Table 1. Synthesis of butylsufinylimines[a]

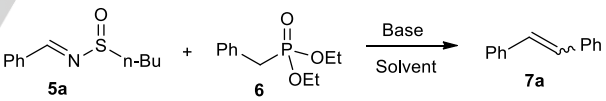
Entry	R	Product	Yields (%) [c]
1	Ph	5a	64
2	4-Cl-C_6H_4	5b	65
3	4-NO_2-C_6H_4	5c	76
4	3-OMe-C_6H_4	5d	57
5	4-Me-C_6H_4	5e	50
6	4-OMe-C_6H_4	5f	48
7	Naphthyl	5g	49
8	4-pyridyl-	5h	55
9	Butyl	5i	51
10	heptyl	5j	47

[a] Reaction conditions: Sulfinamide **3** (1 mmol), aldehyde **4a-j** (1.1 mmol), anhy. $CuSO_4$ (2 mmol), DCM (5 mL), rt, 12h-24h. [b] Isolated yield.

We started our study by optimizing reaction conditions. For that goal, we chose *N*-benzylidenebutane-1-sulfinamide (**5a**) and diethyl benzylphosphonate as the simplest model substrates. We tested a range of bases that are typically used for the preparation of carbanion (table 2). N-butyllithium and LDA in THF at -78 ˚C induced the reaction, albeit in a non-selective manner and leaving unconsumed sulfinylimine (which could be reused later). DBU provided no product at all. Changing the base to sodium hydride in 1,2-dimethoxyethane (DME) allowed for complete conversion and higher yield, as well as stereoselectivity of over 99% towards the *E*-alkene. The solvent imparts great influence on yield and stereochemistry of the reaction. In addition, sodium hydride presents the key advantage of carrying out the reaction at room temperature. The reaction required some excess of the base (2 equiv.) for complete consumption of the starting *N*-sulfinylimine. In addition, a small excess (1.2 mmol) of phosphonate was also used for complete conversion.

The solvent influences the stereochemistry and yield of the product in the reaction. Dimethoxyethane (DME) proved to provide superior reaction yield and geometric control, leading to complete conversion of the starting material and excellent selectivity. Sodium hydride in DME at room temperature overnight proved to be the optimal set of conditions for the reaction of our model substrates giving 85 % isolated alkene.

Table 2. Optimization of reaction conditions[a]

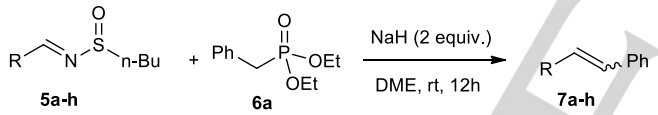


Entry	Base	Solvent	Yield (%) [b]	E:Z ratio [c]
1[d]	n-BuLi	THF	40	50:50
2[e]	LDA	THF	53	56:44
3	NaH	THF	80	90:4
4	DBU	THF	NR	--
5	DBU	DME	NR	--
6	NaH	DME	85	>99:1
7	NaH	ACN	trace	--
8	NaH	DCE	9	--

[a] Reaction conditions: Sulfinylimine (1 mmol), phosphonate (1.2 mmol), NaH (2 equiv.), solvent (2 mL), room temp., 12h. [b] Isolated yields. [c] *E:Z* ratio analysed form NMR spectrum. [d,e] -78 ˚C to rt, THF, 4h.

With our ideal conditions found, (NaH in DME at room temperature) we decided to test the scope of this reaction by changing the electronic conditions in both reagents. First, we looked at electronic effects in the *N*-sulfinylimines, maintaining the same simple benzylphosphonate as a reactant (table 3). As described above, phenylsulfinylimine provides exclusively *E*-stilbene in 85 % isolated yield. The presence of substituents in the phenyl ring of sulfinylimine does not affect the diastereoselectivity of the obtained alkene but it affects reaction yields. A methoxy substituent at the *meta*-position of the imine reduced the isolated yield slightly to 75%. A 4-nitro group (table 3, entry 4) enhanced the reactivity of the imine to give *trans*-alkene in excellent yield. The 4-chloro substituted aryl sulfinylimine produced 1-chloro-4-styrylbenzene in 74 % yield with greater than 99% *E*-geometry. On the other hand, electron-donating effects, such as in the case of a methoxy in the para position (table 3, entry 6) decreases the electrophilicity of the imine, significantly reducing the yield of the reaction (30 % isolated alkene). However, in the case of a methyl group at the 4-position the effect is reduced, and a good yield is obtained (table 3, entry 5). Heteroaryl (e.g.; pyridyl) substituted sulfinylimine also successfully reacted with phosphonate to afford 60 % (*E*)-4-styrylpyridine as only steroisomeric product. Our reaction also tolerated the bulky naphthylsulfinylimine giving only (*E*)-1-styrylnaphthalene in excellent yield. Alkyl substituted sulfinylimines react, albeit in poor yields to substituted styrenes (table 3, entries 7, 8).

Table 3. Survey of stereoelectronic effects on the reaction of *N*-sulfinylimine with Wittig-Horner reagent [a]



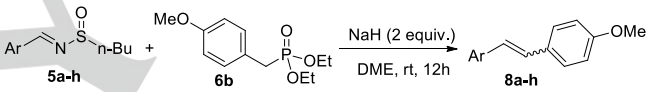
5a-h **6a** **7a-h**

Entry	R	Product	Yield (%) [b]	*E:Z* ratio [c]
1	Ph	**7a**	85	>99:1
2	4-Cl-C_6H_4	**7b**	74	>99:1
3	4-NO_2-C_6H_4	**7c**	88	97:3
4	3-OMe-C_6H_4	**7d**	76	>99:1
5	4-Me-C_6H_4	**7e**	84	>99:1
6	4-OMe-C_6H_4	**7f**	30	>99:1
7	4-pyridyl-	**7g**	60	>99:1
8	Naphthyl	**7h**	85	>99:1
9	Butyl	**7i**	trace	-
10	heptyl	**7j**	29	>99:1

[a] Reaction conditions: Sulfinylimine (1 mmol), benzyl phosphonate (1.2 mmol), NaH (2 equiv.), DME (2 mL), room temp., 12h. [b] Isolated yields. [c] Stereoselective *E:Z* ratio was analyzed by NMR.

Next we tested the impact of an electron-donating substituents in the phosphonate reactant. For this purpose, we prepared diethyl 4-methoxybenzylphosphonate **6b** from reacting 1-(chloromethyl)-4-methoxybenzene with triehtylphosphite.[21] A broad range of electron rich and poor sulfinylimines were reacted with **6b** to provide the corresponding alkenes. Importantly, the electron-donating group reduced the product yields compared to phenylphosphonate **6a**, as 4-OMe group in **6b** decreases the basicity of the α-hydrogen to the phosphonate, leading to an overall conversion of the starting material to the carbanion, as evident by the NMR of the crude reaction mixture. An additional methoxy substituent at 4 position in the imine makes the imine even less reactive in the reaction, providing only traces of the alkene, while methyl substitution afforded moderate yield (table 4, entries 5, 6). Heteroaryl (e.g.; pyridyl) substituted sulfinylimines were completely unreactive under these reaction conditions, whereas electron withdrawing nitro substituent enhanced the reaction yield to 74%. A bulky napthyl group in the sulfinylimine is well tolerated in the reaction and gave reasonable yield in excellent selectivity. Alkyl sulfinylimines were almost unreactive in the reaction, providing trace amounts of the substituted styrenes (table 4, entries 8, 9).

Table 4. Reaction of *N*-sulfinylimine with Electron Donating Wittig-Horner reagent [a]



5a-h **6b** **8a-h**

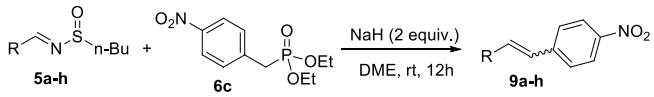
Entry	Ar	Product	Yield (%) [b]	*E:Z* ratio [c]
1	Ph	**8a**	68	>99:1
2	4-Cl-C_6H_4	**8b**	67	>99:1
3	4-NO_2-C_6H_4	**8c**	74	86:14
4	3-OMe-C_6H_4	**8d**	50	>99:1
5	4-Me-C_6H_4	**8e**	49	>99:1
6	4-OMe-C_6H_4	**8f**	trace	-
7	Naphthyl	**8g**	70	>99:1
8	Butyl	**8h**	trace	-
9	Heptyl	**8i**	trace	-
10	4-pyridyl-	**8j**	0	-

[a] Reaction conditions: Sulfinylimine (1 mmol), phosphonate (1.2 mmol), NaH (2 equiv.), solvent (2 mL), rt, 12h. [b] Isolated yield. [c] *E:Z* ratio from NMR.

The effect of electron deficiency in Wittig-Horner reactants was also tested. **6c** containing an electron withdrawing nitro group at the 4 position was prepared and used as a model compound. As expected, the EWG group in **6c** increased the reactivity and therefore the isolated yields, while diastereoselectivity is completely maintained, i.e., *E* alkenes were obtained exclusively. The results in table 5 show good to excellent isolated yields

consistently with aromatic sulfinylimnes (table 5, entries 1-5). Surprisingly, 4-nitro substituted sulfinylimine (table 4, entry 3) was almost unreactive in this reaction, providing only traces of the desired alkene. Electron donating substituents in the imine still resulted in good amounts of the alkene (table 5, entries 5, 6). Again, bulky naphthylsulfinylimine presented no significant problem, providing **9e** in 84 % and 97:3 *E/Z* selectivity. Alkylsulfinylimines were again less reactive, but provided moderate yields of 4-nitrostyrenes with excellent diastereoselectivity (table 5, entries 7, 8).

Table 5. Reaction of *N*-sulfinylimine with Electron Withdrawing Wittig-Horner reagent [a]



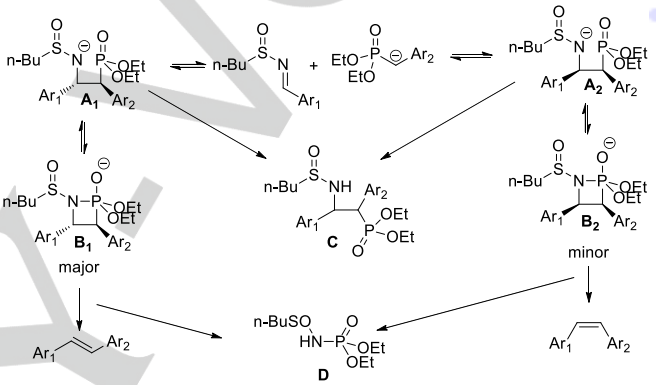
Entry	R	Product	Yield (%) [b]	*E:Z* ratio [c]
1	Ph	**9a**	73	>99:1
2	4-Cl-C_6H_4	**9b**	81	>99:1
3	4-NO_2-C_6H_4	**9c**	trace	-
4	3-OMe-C_6H_4	**9d**	79	>99:1
5	4-Me-C_6H_4	**9e**	66	>99:1
6	4-OMe-C_6H_4	**9f**	75	>99:1
7	Naphthyl	**9g**	84	93:7
8	Butyl	**9h**	52	>99:1
9	heptyl	**9i**	39	>99:1

[a] Reaction conditions: Sulfinylimine (1 mmol), phosphonate (1.2 mmol), NaH (2 equiv.), solvent (2 mL), room temp., 12h. [b] Isolated yield. [c] *E:Z* ratio from NMR.

Based on the results observed and the vast knowledge on the Wittig-Horner reaction, we propose a similar mechanism for the olefination of *N*-sulfinylimines.[15] After deprotonation, the phosphonate carbanion adds in a reversible way to the imine, with fast conversion between *syn* (**A_2**) and *anti* (**A_1**) intermediate. Given the steric hindrance in **A_2**, **A_1** exists in higher concentrations. Ring closing to azaphosphatidin **B** then occurs at the rate-determining step, followed by the irreversible ring opening to the desired alkenes and diethyl (butylthio)oxyphosphoramidate **D** (Scheme 4). Alkylphosphonates (e.g; diethyl butylphosphonate) provide low conversions to the the desired styrene. The reason for that is that **A** is more basic and the reaction is directed towards *N*-sulfinamidophosphonate **C** by proton abstraction. Formation of **C** is clearly seen by NMR analysis of crude reaction mixture.

Conclusions

In summary, we have tested and optimized the Wittig-Horner-Emmons reaction reaction of *N*-sulfoxide stabilised imines, accomplishing the diastereoselective conversion of an important chiral auxiliary into useful 1,2-disubstituted alkenes which can be used to further functionalize the molecule. A broad range of easily accessible aromatic and aliphatic *N*-sulfinylimines react with electronically diverse arylphosphonates to give 1,2-disubtituted alkenes in moderate to good yield and almost complete *E*-selectivity. In contrast, alkylphosphonate was unsuccessful in these reactions, providing *N*-sulfonamidophosphonates. Stereoselective addition of the phosphonate to the *N*-sulfinylimine governs the geometric outcome of the alkene, favouring *E*-selective alkenes.



Scheme 4: Proposed Mechanism of the Olefination reaction

Experimental Section

General Remarks All materials, unless otherwise stated, were purchased from commercial sources and utilized without further purification. Flash column chromatography was conducted with silica gel 60 (230-400 mesh) from Merck. All ^{1}H and ^{13}C NMR spectra were recorded using an AVANCE II 300 MHz and 400 MHz Bruker spectrometer at the Technion NMR facilities. Chemical shifts (δ) are reported in ppm, relative to residual $CHCl_3$ as an internal reference (^{1}H, 7.26 ppm; ^{13}C, 77.16 ppm). Coupling constants (J) are reported in hertz (Hz). Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). High-resolution mass spectrometry was done in a Waters LCT Premier Mass Spectrometer, Waters ACQUITY UPLC System: ESI+, MeCN: H_2O (70:30) 0.25 mL/min.

General Procedure

Preparation of Sulfinamide:[22] In a 100 mL round bottom flask 1-bromobutane (2.534 g, 18.5 mmol) and potassium thioacetate (4.05 g, 35.4 mmol) were refluxed in THF (50 mL) overnight. Solvent was removed under reduced pressure and the remaining dissolved in ethylacetate. The organic phase was washed with saturated $NaHCO_3$ solution (50 mL), and then the

aqueous phase was extracted with ethylacetate (3 x 50 mL). The combined organic phase was evaporated to provide the pure thioacetate **1** (2.44 g, quantitative) as a brown liquid. Compound **1** (2.44 g, 18 mmol) was dissolved in DCE (10 mL). Then, Ac_2O (1.92 mL, 20. 2 mmol) and SO_2Cl_2 (3.1 mL, 42.4 mmol) were added at -10 °C and stirred for 30 min. The mixture was then allowed to return to rt and the solvent was evaporated to a brown oil. The oil was dissolved in CH_2Cl_2 and poured into ice cold aqueous NH_4OH solution (8 mL). The organic phase was separated and the aqueous layer further extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phase was evaporated to provide pure sulfinamide **2** as an orange yellow liquid, 1.65 g, 72% yield. **S-butyl ethanethioate (1)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.75 (dd, *J* = 8.7, 5.7 Hz, 2H), 2.20 (d, *J* = 4.5 Hz, 3H), 1.42 (dd, *J* = 14.7, 7.5 Hz, 2H), 1.27 (dd, *J* = 14.2, 7.1 Hz, 2H), 0.79 (dd, *J* = 8.9, 5.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 31.4, 30.3, 28.6, 21.7, 13.4; **Butane-1-sulfinamide** (**2**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.03 – 2.78 (m, 1H), 2.41 (dd, *J* = 27.5, 14.7 Hz, 1H), 1.69 (dd, *J* = 30.9, 23.4 Hz, 2H), 1.51 – 1.21 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.3, 25.0, 21.5, 13.5.

Preparation of *N*-Sulfinylimines 5:[23] In a 50 mL round bottom flask, butylsulfinamide **2** (121 mg, 1 mmol) and aldehyde (1.2 mmol) were dissolved in CH_2Cl_2 (5 mL). Then, anhydrous $CuSO_4$ (351 mg, 2.2 mmol) was added and the mixture refluxed for 12 h. The reaction mixture was then filtered and the solids washed with CH_2Cl_2. The organic layer was dries over anhydrous $MgSO_4$. The solvent was evaporated and crude product purified by column chromatography over silica gel.

(*E*)-*N*-benzylidenebutane-1-sulfinamide (5a): Yellow liquid; 64% yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.85 – 7.75 (m, 2H), 7.55 – 7.38 (m, 3H), 2.94 (ddd, *J* = 13.1, 9.7, 6.1 Hz, 1H), 2.74 – 2.60 (m, 1H), 1.83 – 1.69 (m,1H), 1.69 – 1.59 (m, 1H), 1.44 (dtd, *J* = 15.4, 7.2, 3.2 Hz, 2H), 0.93 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 133.8, 132.4, 129.3 (2C), 128.9 (2C), 55.2, 23.0, 21.8, 13.6; HRMS (ESI) m/z 210.0952, (calcd. $C_{11}H_{16}NOS^+$, 210.0947).

(*E*)-*N*-(4-chlorobenzylidene)butane-1-sulfinamide (5b): Yellow liquid; 65% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (s, 1H), 7.79 – 7.69 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 2.93 (ddd, *J* = 13.1, 9.6, 6.1 Hz, 1H), 2.68 (ddd, *J* = 13.1, 9.6, 5.4 Hz, 1H), 1.75 (ddd, *J* = 9.3, 6.9, 4.0 Hz, 1H), 1.70 – 1.60 (m, 1H), 1.48 – 1.39 (m, 2H), 0.94 – 0.87 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 138.6, 132.2, 130.4 (2C), 129.2(2C), 55.2, 23.0, 21.8, 13.6; HRMS (ESI) m/z 244.0543, (calcd. $C_{11}H_{15}ClNOS^+$, 244.0557).

(*E*)-*N*-(4-nitrobenzylidene)butane-1-sulfinamide (5c): Light Yellow Solid, 76% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.30 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 2.98 (ddd, *J* = 13.1, 9.7, 6.1 Hz, 1H), 2.73 (ddd, *J* = 13.1, 9.7, 5.4 Hz, 1H), 1.87 – 1.71 (m, 1H), 1.71 – 1.54 (m, 1H), 1.54 – 1.35 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 149.7, 138.6, 130.0 (2C), 124.1 (2C), 55.1, 23.1, 21.8, 13.6; HRMS (ESI) m/z 255.0803, (calcd. $C_{11}H_{15}N_2O_3S^+$, 255.0798).

(*E*)-*N*-(3-methoxybenzylidene)butane-1-sulfinamide (5d): Yellow liquid; 57% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.38 – 7.25 (m, 3H), 7.06 – 6.92 (m, 1H), 3.77 (s, 3H), 2.89 (ddd, *J* = 13.1, 9.7, 6.1 Hz, 1H), 2.64 (ddd, *J* = 13.1, 9.6, 5.4 Hz, 1H), 1.71 (dd, *J* = 10.6, 4.3 Hz, 1H), 1.66 – 1.54 (m, 1H), 1.49 – 1.33 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 159.8, 135.0, 129.8, 122.5, 118.9, 112.7, 55.2, 55.1, 22.95, 21.8, 13.6; HRMS (ESI) m/z 240.1061, (calcd. $C_{12}H_{18}NO_2S^+$, 240.1053).

(*E*)-*N*-(4-methylbenzylidene)butane-1-sulfinamide (5e): Yellow liquid; Yield 50%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 2.94 (ddd, *J* = 13.1, 9.7, 6.1 Hz, 1H), 2.69 (ddd, *J* = 13.1, 9.7, 5.4 Hz, 1H), 2.40 (s, 3H), 1.78 (tdd, *J* = 15.5, 9.5, 6.2 Hz, 1H), 1.69 – 1.59 (m 1H), 1.47 (ddd, *J* = 10.4, 7.9, 2.9 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). HRMS (ESI) m/z 240.1091; (calcd. $C_{12}H_{18}NOS^+$, 224.1104).

(*E*)-*N*-(4-methoxybenzylidene)butane-1-sulfinamide (5f): Yellow liquid; Yield 48%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.81 – 7.71 (m, 2H), 7.00 – 6.93 (m, 2H), 3.85 (s, 3H), 2.92 (ddd, *J* = 13.1, 9.7, 6.1 Hz, 1H), 2.67 (ddd, *J* = 13.1, 9.6, 5.5 Hz, 1H), 1.85 – 1.69 (m, 1H), 1.69 – 1.61 (m, 1H), 1.46 (ddd, *J* = 8.5, 7.1, 4.2 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 160.8, 131.2 (2C), 127.0, 114.6, 114.2 (2C), 55.4, 23.0, 21.8, 13.6; HRMS (ESI) m/z 240.1091; (calcd. $C_{12}H_{18}NO_2S^+$, 240.1053).

(*E*)-N-(naphthalen-1-ylmethylene)butane-1-sulfinamide (5g): Yellow liquid; 49% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.17 (s, 1H), 8.98 (d, *J* = 8.3 Hz, 1H), 8.00 (dd, *J* = 12.5, 5.0 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.48 (m, 3H), 3.02 (ddd, *J* = 13.1 9.8, 6.1 Hz, 1H), 2.89 – 2.69 (m, 1H), 1.85 – 1.68 (m, 2H), 1.52 – 1.38 (m, 2H), 0.99 – 0.89 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 133.8, 133.3, 131.7, 131.1, 129.1, 128.8, 127.9, 126.4, 125.1, 124.2, 55.5, 23.1, 21.9, 13.7; HRMS (ESI) m/z 260.1111, (calcd. $C_{15}H_{18}NOS^+$, 260.1104).

(*E*)-*N*-(pyridin-4-ylmethylene)butane-1-sulfinamide (5h): Yellow liquid; 55% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.6 Hz, 2H), 8.55 (s, 1H), 7.74 – 7.56 (m, 2H), 2.94 (ddd, *J* = 13.1, 9.6, 6.1 Hz, 1H), 2.69 (ddd, *J* = 13.1, 9.7, 5.4 Hz, 1H), 1.85 – 1.67 (m, 1H), 1.67 – 1.53 (m, 1H), 1.53 – 1.34 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 150.7 (2C), 139.9, 122.4 (2C), 55.0, 23.0, 21.4, 13.6; HRMS (ESI) m/z 211.0901, (calcd. $C_{10}H_{15}N_2OS^+$, 211.0900).

(*E*)-*N*-butylidenebutane-1-sulfinamide (5i): Yellow liquid; 51% yield; ^{1}H NMR (200 MHz, $CDCl_3$) d 8.08 (t, *J* = 4.8 Hz, 1H), 2.92 – 2.79 (m, 1H), 2.58 (dd, *J* = 6.6, 2.9 Hz, 1H), 2.47 (dt, *J* = 7.5, 3.6 Hz, 2H), 1.76 – 1.56 (m, 4H), 1.45 (dd, *J* = 7.1, 2.2 Hz, 2H), 0.96 (q, *J* = 7.3 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 168.5, 55.1, 37.9, 23.0, 21.9, 18.9, 13.7 (2C); HRMS (ESI) m/z 176.1004, (calcd. $C_8H_{18}NOS^+$, 176.1104).

(*E*)-*N*-heptylidenebutane-1-sulfinamide (5j): Yellow liquid; 47% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (t, *J* = 4.8 Hz, 1H), 2.76 (ddd, *J* = 13.2, 9.6, 6.1 Hz, 1H), 2.53 – 2.46 (m, 1H), 2.44 –

2.36 (m, 3H), 1.58 – 1.47 (m, 4H), 1.42 – 1.31 (m, 3H), 1.24 – 1.18 (m, 5H), 0.84 – 0.74 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 54.9, 35.8, 31.3, 28.6, 25.2, 22.8, 22.3, 21.7, 13.8, 13.5; HRMS (ESI) m/z 218.1677, (calcd. $C_{11}H_{24}NOS^+$, 218.1573).

General procedure for Olefination reaction with *N*-Sulfinylimine: In a 25 mL round bottom flask NaH (20 mg of NaH in 60% in oil, 2 mmol) was weighted and washed with hexane. Then, arylphosphonate (1.2 mmol) was added dissolved in dry DME (2 mL) and stirred for 30 min (effervescence is observed). To this mixture, sulfinylimine (1 mmol) in DME (1 mL) was added and the reaction stirred at rt for 12 h. The reaction was then quenched with water and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure to get the product as a crude oil. Purification was done by column chromatography over silica gel.

(*E*)-1,2-diphenylethene (7a): White solid; Yield 85%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.4 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 4H), 7.25 (dd, *J* = 9.7, 4.8 Hz, 2H), 7.11 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2 (C), 128.6 (CH), 127.53 (CH), 126.41 (CH). All the spectral data in accordance with literature report.[24]

(*E*)-1-chloro-4-styrylbenzene (7b): White solid; Yield 74%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.24 (m, 9H), 7.05 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 135.7, 133.1, 129.2, 128.7, 128.6, 127.7, 127.6; 127.3, 126.4; All the spectral data in accordance with literature report.[25]

(*E*)-1-nitro-4-styrylbenzene (7c): Yellow solid; Yield 88%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 6.5, 4.7 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.56 – 7.51 (m, 2H), 7.40 – 7.28 (m, 3H), 7.23 (d, *J* = 2.8 Hz, 1H), 7.12 (d, *J* = 16.4 Hz, 1H). All the spectral data in accordance with literature report.[26]

(*E*)-1-methoxy-3-styrylbenzene (7d): Yellow oil; Yield 76%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 6.9, 1.3 Hz, 2H), 7.43 – 7.23 (m, 4H), 7.18 – 7.04 (m, 4H), 6.89 – 6.78 (m, 1H), 3.87 (s, 3H). All the spectral data in accordance with literature report. [27]

(*E*)-1-methyl-4-styrylbenzene (7e): White solid; yield 84%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.25 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 1.3 Hz, 2H), 2.36 (s, 3H). All the spectral data in accordance with literature report. [28]

(*E*)-1-methoxy-4-styrylbenzene (7f): White solid; Yield 30%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 4H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.15 (m, 1H), 7.11 – 6.96 (m, 2H), 6.96 – 6.85 (m, 2H), 3.82 (s, 3H). All the spectral data in accordance with literature report.[29]

(*E*)-4-styrylpyridine (7g): Colourless oil; Yield 60%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 2H), 7.52 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.36 – 7.23 (m, 6H), 7.00 (d, *J* = 16.3 Hz, 1H). All the spectral data in accordance with literature report.[30]

(*E*)-1-styrylnaphthalene (7h): Yellow oil; Yield 85%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.9 Hz, 1H), 7.93 – 7.84 (m, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.58 – 7.45 (m, 3H), 7.41 (dd, *J* = 10.1, 4.7 Hz, 2H), 7.28 (ddd, *J* = 11.4, 8.4, 1.6 Hz, 1H), 7.15 (d, *J* = 16.0 Hz, 1H). All the spectral data in accordance with literature report.[31]

(*E*)-1-methoxy-4-styrylbenzene (8a): Yellow solid; Yield 68%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 3H), 7.09 – 6.94 (m, 2H), 6.89 (dd, *J* = 9.5, 7.4 Hz, 2H), 3.81 (s, 3H). All the spectral data in accordance with literature report.[26]

(*E*)-1-chloro-4-(4-methoxystyryl)benzene (8b): Yellow liquid; Yield 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 13.1, 8.6 Hz, 3H), 7.26 – 7.16 (m, 3H), 6.96 (d, *J* = 16.3 Hz, 1H), 6.88 – 6.78 (m, 3H), 3.76 (s, 3H). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[32]

(*E*)-1-methoxy-4-(4-nitrostyryl)benzene (8c): Yellow solid; Yield 74%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 17.3 Hz, 1H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.93 – 6.86 (m, 2H), 3.83 (s, 3H). All the spectral data in accordance with literature report.[33] ***Z*-isomer**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.79 – 6.68 (m, 2H), 6.49 (d, *J* = 12.1 Hz, 2H), 3.77 (s, 2H).

(*E*)-1-methoxy-3-(4-methoxystyryl)benzene (8d): White solid; Yield 50%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.7 Hz, 2H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.12 – 7.05 (m, 1H), 7.01 (s, 2H), 6.95 (s, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.78 (dd, *J* = 8.1, 2.5 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H). All the spectral data in accordance with literature report.[34]

(*E*)-1-methoxy-4-(4-methylstyryl)benzene (8e): White solid; Yield 49%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 16.0, 8.4 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 4H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.34 (s, 3H). All the spectral data in accordance with literature report.[34]

(*E*)-1-(4-methoxystyryl)naphthalene (8g): Yellow liquid; Yield 70%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 – 8.18 (m, 1H), 7.92 – 7.83 (m, 1H), 7.79 (d, *J* = 5.0 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.59 – 7.44 (m, 5H), 7.11 (d, *J* = 16.0 Hz, 1H), 7.00 – 6.91 (m, 2H), 3.84 (s, 3H). All the spectral data in accordance with literature report.[35]

(*E*)-1-nitro-4-styrylbenzene (9a): Yellow liquid; Yield 73%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.45 – 7.28 (m, 3H), 7.23 (d, *J* = 2.5 Hz, 1H), 7.12 (d, *J* = 16.3 Hz, 1H). All the spectral data in accordance with literature report.[26]

(*E*)-1-chloro-4-(4-nitrostyryl)benzene (9b): Yellow Solid; Yield 81%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.6 Hz,

2H), 7.27 – 7.13 (m, 1H), 7.09 (d, *J* = 16.4 Hz, 1H). All the spectral data in accordance with literature report.[36]

(*E*)-1-methoxy-3-(4-nitrostyryl)benzene (9d): Yellow liquid; Yield 79%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.28 (dd, *J* = 15.9, 7.9 Hz, 1H), 7.19 (s, 1H), 7.12 (t, *J* = 3.7 Hz, 2H), 7.06 (dd, *J* = 4.9, 2.7 Hz, 1H), 6.94 – 6.81 (m, 1H), 3.84 (s, 3H). All the spectral data in accordance with literature report.[37]

(*E*)-1-methyl-4-(4-nitrostyryl)benzene (9e): Yellow solid; Yield 66%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 5.5 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 16.3 Hz, 1H), 2.36 (s, 3H). All the spectral data in accordance with literature report.[38]

(*E*)-1-methoxy-4-(4-nitrostyryl)benzene (9f): Yellow solid; Yield 75%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.28 – 7.14 (m, 1H), 6.98 (d, *J* = 16.3 Hz, 1H), 6.94 – 6.86 (m, 2H), 3.83 (s, 3H). All the spectral data in accordance with literature report.[33]

(*E*)-1-(4-nitrostyryl)naphthalene (9g): Yellow Solid; Yield 84%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 8.18 (d, *J* = 7.9 Hz, 1H), 8.04 (d, *J* = 16.0 Hz, 1H), 7.87 (dd, *J* = 9.9, 8.1 Hz, 2H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.60 – 7.45 (m, 2H), 7.18 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ143.9, 133.7, 133.6, 131.2, 130.3, 129.5,129.2, 129.1, 128.7, 126.9 (2C), 126.4, 126.0, 125.5, 124.1 (2C), 124.0, 123.3. All the spectral data in accordance with literature report.[39]

(*E*)-1-nitro-4-(pent-1-en-1-yl)benzene (9h): Yellow Solid; Yield 52%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 6.41 (t, *J* = 3.7 Hz, 2H), 2.21 (tdd, *J* = 7.5, 3.8, 1.4 Hz, 2H), 1.61 – 1.41 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). All the spectral data in accordance with literature report.[40]

(*E*)-1-nitro-4-(oct-1-en-1-yl)benzene (9i): Yellow Solid; Yield 39%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.9 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 2H), 6.41 (s, 2H), 2.33 – 2.12 (m, 2H), 1.45 (dd, *J* = 14.5, 7.2 Hz, 2H), 1.37 – 1.23 (m, 6H), 0.87 (dd, *J* = 9.1, 4.2 Hz, 3H). All the spectral data in accordance with literature report.[41]

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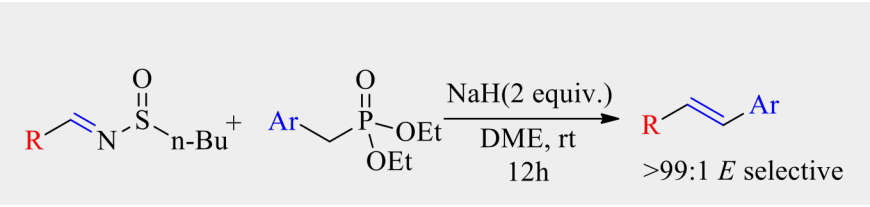
Layout 2:

FULL PAPER



Imines are highly useful directing groups, and coupled with a chiral auxiliary such as sulfoxide group, a powerful tool in total synthesis. Here we show that these groups can be converted in a very efficient diastereoselective route to 1,2-disubstituted alkenes (>99:1 *E* isomer) under very mild conditions.

Diastereoselective Olefination

Shubhendu Dhara[a] and Charles E. Diesendruck *[a]

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Olefination of *N*-Sulfinylimines under Mild Conditions