Tetrahedron Letters 51 (2010) 6227–6231

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

One-pot synthesis of stilbenes by dehydrohalogenation–Heck olefination and multicomponent Wittig–Heck reaction

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ARTICLE INFO

Article history:
Received 2 August 2010
Revised 7 September 2010
Accepted 10 September 2010
Available online 17 September 2010

Keywords:
Heck reaction
In situ generation of styrene
One-pot multicomponent reactions
Dehydrohalogenation–Heck
Wittig–Heck

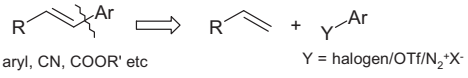
ABSTRACT

A variant of olefination reaction involving in situ generation of styrene by either one-pot dehydrohalogenation–Heck or one-pot multicomponent Wittig–Heck reaction is developed.

The concept of performing more than one transformation in a single vessel, or developing one-pot processes, can generate less waste, reduce work-up procedures, avoid separation of unstable intermediates, save time and energy, and increase the efficiency of the desired conversion.[1] Since its discovery the Mizoroki–Heck reaction,[2] which involves palladium catalyzed coupling of aryl halide and styrene, remains the best method for preparation of stilbene derivatives. This method has been a subject of extensive research, while it has been used for the synthesis of a large number of natural and artificial molecules.[3] In most cases the reaction is done with suitable aryl halide and a styrene or similar olefin in the presence of small quantity of Pd-catalyst and stoichiometric amount of a base. Usually the aryl halide or in some cases aryl triflate[4] and aryl diazonium salt[5] are easily obtained either from a commercial source or prepared by known methods. The other component is usually a styrene or a derivative of acrylic acid/acrylonitrile etc. Scheme 1.

Although, the Mizoroki–Heck reaction has proved its effectiveness, the synthetic utility purely depends on the availability of these components. Usually ArBr, ArI, ArOTf, and $ArN_2^+X^-$ are relatively easy to prepare or are readily available. On the other hand, in many cases the other components, alkenes, are not readily available; either they are difficult to prepare or tricky to purify due to their tendency to polymerize during distillation or storage. Even under usual high reaction temperature conditions there is a possibility of polymerization and hence, it is used in excess. The latter problem can be solved if the olefin is somehow synthesized in situ during the Mizoroki–Heck reaction. There are a few reported examples of one-pot combination of synthesis of substituted olefins.[6–13] These include synthesis of olefins via Hunsdiecker reaction,[6] Knoevenagel-decarboxylation sequence,[9] Mizoroki–Heck, Wittig reaction,[11] or four component Ugi–Heck sequence.[12]

In this letter we present two one-pot methods consisting of olefination processes and the Mizoroki–Heck reaction. The prerequisite of planning the one-pot multi-step reactions is the compatibility of the reagent system and reaction conditions. In the present effort the second reaction, the Mizoroki–Heck is carried out with Pd-catalyst and a suitable base. Taking this into consideration the required olefin can be either synthesized by base mediated dehydrohalogenation of suitable alkyl halide or by Wittig reaction from aldehyde and appropriate phosphonium salt. The two approaches are outlined in Scheme 2 taking the example of the in situ synthesis of styrene **1** and then subjected to Mizoroki–Heck conditions to form stilbene **2**. In the approach **A-1** the styrene is prepared by dehydrohalogenation of (2-bromoethyl)benzene **3**, and in **A-2** from (1-bromoethyl)benzene **4** using the same base which also facilitates subsequent Mizoroki–Heck reaction. Reaction of **3** may be more favorable compared to **4** if it follows the E1cB mechanism[14] and hence, the availability of styrene will be more for further Mizoroki–Heck reaction.



Scheme 1. Disconnection approach for stilbene or similar molecules.

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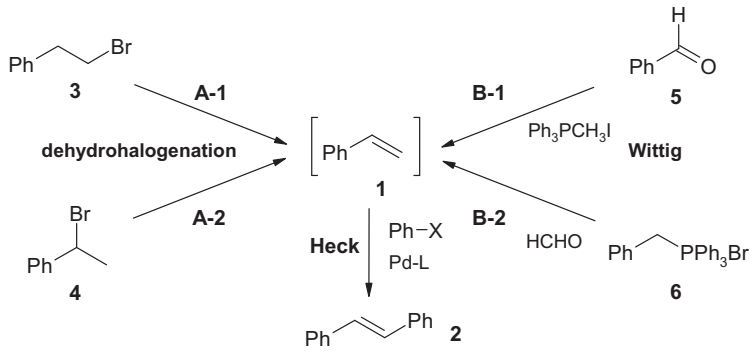
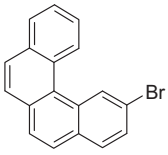
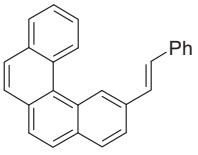
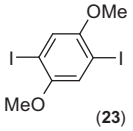
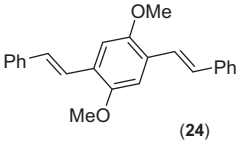
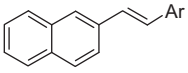
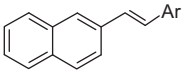
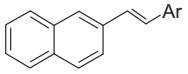
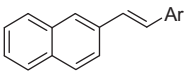
doi:10.1016/j.tetlet.2010.09.050



Scheme 2. Proposed routes of in situ synthesis of styrene for subsequent one-pot Heck reaction.

Alternatively the intermediate styrene may be prepared by Wittig reaction of an aldehyde and suitable phosphonium salt (approach **B** of Scheme 2). Since the Wittig reaction involves two components, that is, an aldehyde and a phosphonium salt, synthesis of styrene can be achieved either by approach **B-1** using benzaldehyde **5** and phosphonium salt obtained from methyl iodide or

Table 1
Synthesis of stilbenes with one-pot two component procedure of dehydrohalogenation-Heck reaction

Entry	Alkyl halide (1.0 equiv)	Aryl halide (1.2 equiv)	Olefin obtained	Yield[a] (%)
1	**3**	Iodobenzene (**13**)	*trans*-Stilbene (**14**)	80 (66)[b] (54)[c]
2	**4**	Iodobenzene (**13**)	*trans*-Stilbene (**14**)	67
3	**3**	4-Iodoanisole (**15**)	*trans*-4-Methoxystilbene (**16**)	54
4	**3**	1-Bromo-4-nitrobenzene (**17**)	*trans*-4-Nitrostilbene (**18**)	67
5	**3**	1-Bromo-3-nitrobenzene (**19**)	*trans*-3-Nitrostilbene (**20**)	78
6	**3**	 (**21**)	 (**22**)	69
7	**3**	 (**23**)	 (**24**)	74
8	**4**	4-Iodoanisole (**15**)	*trans*-4-Methoxystilbene (**16**)	84
9	**4**	1-Bromo-4-nitrobenzene (**17**)	*trans*-4-Nitrostilbene (**18**)	80
10	**11**	Iodobenzene (**13**)	 (**25**, Ar = C_6H_5)	64
11	**11**	4-Iodoanisole (**15**)	 (**26**, Ar = 4-$MeOC_6H_4$)	86
12	**11**	4-Iodoacetanilide (**27**)	 (**28**, Ar = 4-$AcNHC_6H_4$)	54
13	**11**	4-Bromo chlorobenzene (**29**)	 (**30**, Ar = 4-ClC_6H_4	88
14	**12**	Iodobenzene (**13**)	*trans*-4-Nitrostilbene (**18**)	76
15	**12**	4-Iodo anisole (**15**)	*trans*-1-(4-Methoxystyryl)-4-nitrobenzene (**31**)	77

All reactions run with aryl halide (1 equiv), alkyl halide (1.2 equiv), K_2CO_3 (3 equiv), $Pd(OAc)_2$ (0.5%), **7** or **8** (0.55%) in DMA at 140 °C for 40 h. For entry 7:**3** (3 equiv), K_2CO_3 (4 equiv), Pd (1.0%)-**8** (2.5%).

[a] Isolated Yield.
[b] With L-**10**.
[c] With L-**9**.

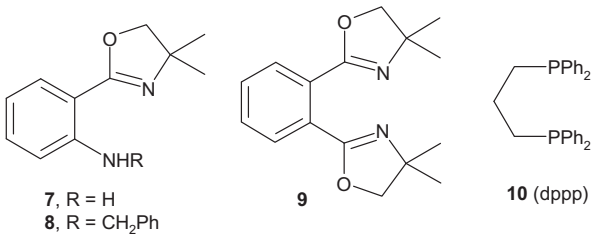


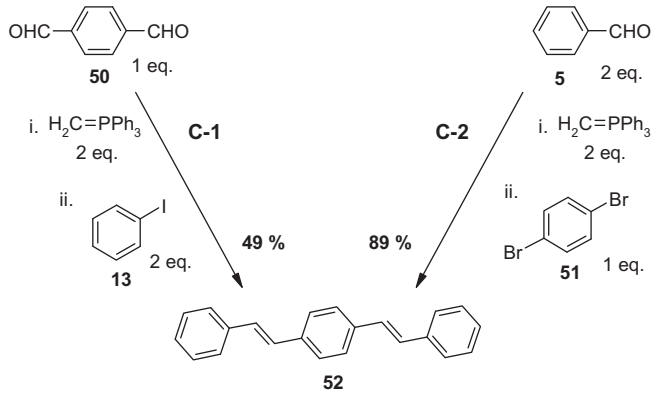
Figure 1. Ligands investigated for the present study.

by **B-2** using formaldehyde and phosphonium salt **6** obtained from benzyl bromide and triphenylphosphine.

Several ligands were chosen for the present Mizoroki–Heck reaction as shown in Figure 1. There is considerable interest in screening phosphine free ligands for Pd mediated Mizoroki–Heck reaction,[15] whereas **7** and **8** were synthesized as per the reported procedures.[16]

In order to demonstrate the generality of this approach (A), a series of alkyl bromides are prepared to access a variety of stilbenes and are listed in Figure 2. The mixture of suitable aryl halide, an alkyl halide, an excess of K_2CO_3, catalytic quantity of $Pd(OAc)_2$-ligand in dry DMA was heated at 140 °C. Careful TLC analysis indicated the formation of corresponding stilbene, which was isolated and characterized. The results are presented in Table 1.

In most of the cases the isolated yields of olefin are good with just 1.2 equiv of alkyl halide. As expected the formation of *trans*-stilbene **14** from alkyl halide **3** was more favored than from alkyl halide **4**, due to the more facile elimination process. However, it will be more logical and practical to use alkyl halides of the type **4** and **11**, as they are more readily accessed from ethyl aryls by benzylic bromination condition [NBS-Bz_2O_2-light], as we did.



Scheme 3. One-pot five-component approach for 1,4-distyryl benzene **52**.

The second approach involves the in situ synthesis of styrenes by the classical Wittig olefination.[17] Reaction of aromatic aldehyde with phosphonium salts undergoes Wittig reaction even with weak base like potassium carbonate,[18] a typical base for Mizoroki–Heck reaction. Hence an equimolar amount of benzaldehyde, $Ph_3P^+CH_3I^-$, iodobenzene, excess of K_2CO_3, catalytic quantity of $Pd(OAc)_2$·oxazolinyl ligand **7** or **8**, TBAB as PTC was heated in DMF and we found the formation of *trans*-stilbene in good yield. Further experimentation demonstrated that this concept is clearly reproducible for a number of aldehydes, three representative phosphonium salts, and another set of aryl halides (Table 2). One carbon aldehyde unit was accessed by employing *para*-formaldehyde (0.34 equiv) in the reaction and hence, the same number of variations was available for the facile generation of substituted stilbenes. Utilizing the well established, transition metal free, high yielding Wittig reaction for

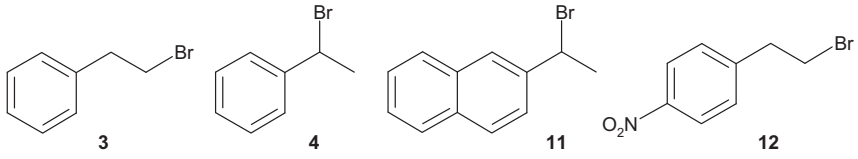


Figure 2. Alkyl halides used for in situ generation of olefins by dehydrohalogenation for Mizoroki–Heck reaction.

Table 2
Synthesis of stilbenes by one-pot three component procedure of Wittig–Heck reaction

Entry	Aldehyde (1 equiv)	Phosphonium salt (1 equiv)	Aryl halide (1 equiv)	Olefin	Yield[a] (%)
1	Benzaldehyde (**5**)	$Ph_3P^+CH_3\ I^-$	Iodobenzene (**13**)	*trans*-Stilbene (**14**)	91[b]
2	4-Nitrobenzaldehyde (**32**)	$Ph_3P^+CH_3\ I^-$	Iodobenzene (**13**)	*trans*-4-Nitrostilbene (**18**)	94 (85)[c]
3	4-Chloro benzaldehyde (**33**)	$Ph_3P^+CH_3\ I^-$	Iodobenzene (**13**)	*trans*-4-Chlorostilbene (**34**)	90
4	4-Anisaldehyde (**35**)	$Ph_3P^+CH_3\ I^-$	Iodobenzene (**13**)	*trans*-4-Methoxystilbene (**16**)	88
5	4-*N*,*N*-Dimethylamino benzaldehyde (**36**)	$Ph_3P^+CH_3\ I^-$	Iodobenzene (**13**)	*trans*-4-(*N*,*N*-Dimethylamino) –stilbene (**37**)	83
6	4-Methyl benzaldehyde (**38**)	$Ph_3P^+CH_3\ I^-$	Iodobenzene (**13**)	*trans*-4-Methylstilbene (**39**)	97
7	3-Pyridine carboxaldehyde (**40**)	$Ph_3P^+CH_3\ I^-$	Iodobenzene (**13**)	*trans*-3-Styrylpyridine (**41**)	90
8	Piperonal (**42**)	$Ph_3P^+CH_3\ I^-$	Iodobenzene (**13**)	*trans*-1-(3,4-Methylenedioxyphenyl)-2-phenylethene (**43**)	92
9	4-Chloro benzaldehyde (**33**)	$Ph_3P^+CH_3\ I^-$	4-Iodoanisole (**15**)	*trans*-1-(4-Chlorostyryl)-4-methoxybenzene (**44**)	82
10	4-Anisaldehyde (**35**)	$Ph_3P^+CH_3\ I^-$	1-Bromo-4-nitrobenzene (**17**)	*trans*-1-(4-Methoxystyryl)-4-nitrobenzene (**31**)	82
11	2-Furaldehyde (**45**)	$Ph_3P^+CH_3\ I^-$	Iodobenzene (**13**)	*trans*-2-Styrylfuran (**46**)	82
12	Paraformaldehyde (**47**)	$PhCH_2P^+Ph_3\ Cl^-$	Iodobenzene (**13**)	*trans*-Stilbene (**14**)	88
13	Paraformaldehyde (**47**)	$4\text{-}BrC_6H_4CH_2P^+Ph_3\ Br^-$	4-Iodoanisole (**15**)	*trans*-1-(4-Bromostyryl)-4-methoxybenzene (**48**)	56
14	Paraformaldehyde (**47**)	$4\text{-}BrC_6H_4CH_2P^+Ph_3\ Br^-$	1-Bromo-4-nitrobenzene (**17**)	*trans*-1-(4-Bromostyryl)-4-nitro benzene (**59**)	67

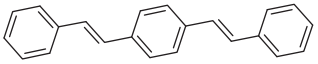
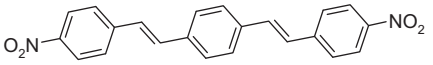
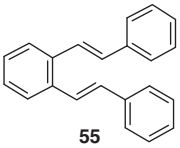
All reactions were run in DMA, with $Pd(OAc)_2$ (0.5 mol %), ligand **7** or **8** (1.0 mol %), K_2CO_3 (3.5 equiv), TBAB (20%) at 130–140 °C for 40 h.

[a] Isolated yield.

[b] With L-**10**.

[c] With L-**9**.

Table 3
One-pot multi component Wittig–Heck approach for distyryl benzene[a]

No	Conditions	Approach (scheme-5)	Distyryl benzene	Yield (%)
1	**50** (1.0 equiv), **13** (2 equiv), Pd (1.0%), **7** (2%)	**C-1**	 **52**	49
2	**51** (1.0 equiv), **5** (2.0 equiv), Pd (1.0%), dppp **10** (2.0%)	**C-2**	**52**	89
3	**51** (1.0 equiv), **5** (2.0 equiv), Pd (1.0%), **7** (2.0%)	**C-2**	**52**	85
4	**51** (1.0 equiv), **32** (2.0 equiv), Pd (1.0%), **7** (2.0%)	**C-2**	 **53**	63
5	**54** (1.0 equiv), **5** (2.0 equiv), Pd (1.0%), **7** (2.0%)	**C-2**	 **55**	77

[a] With $H_2C{=}PPh_3$ (2.0 equiv), TBAB (40%), K_2CO_3 (7 equiv), 140 °C, 48 h. **54** = 1,2-dibromobenzene.

the in situ olefination is an attractive option. It is notable that good yields of olefins are obtained from equimolar mixture of three reagents, compared to the normal Mizoroki–Heck reaction protocol which often requires excess olefin.

The molecules with alternate double bonds and aromatic rings have received substantial attention.[19,20] Our new strategy can be further extended to the synthesis of distyryl benzenes from easily available stable starting materials. The approach involves simultaneous formation of two double bonds between three aromatic rings via a combination of Wittig and Mizoroki–Heck reaction between five reactant molecules in a single step process. This one-pot five-component process can be done in two ways. The 1,4-divinyl benzene was prepared in situ by the reaction of terephthalaldehyde **50** and 2 equiv of Wittig reagent and subsequently subjected into the Pd catalyzed Heck reaction with 2 equiv of iodobenzene (approach **C-1**, Scheme 3) or by making twofold excess of styrene with 1,4-dibromo benzene **51** (approach **C-2**, Scheme 3). The combined yield of the reactions conducted in a single pot was very good, either with ligand **7** or with ligand **8** and with dppp, **10**, Table 3.

The route involving in situ synthesis of 1,4-divinyl benzene from terephthalaldehyde (route **C-1**, Scheme 3) was less effective because of its tendency of cross linking polymerization.

The two one-pot multi-step procedures developed herein[21] have the advantage of using reduced number of work-up and purification steps, adequate chemical yield, and avoiding waste due to polymerization of intermediates.

Acknowledgments

We wish to thank the Gujarat Narmada Fertilizer Corporation (GNFC, Bharuch, India) for the financial assistance for this work. We are grateful to Professor B.V. Kamath and Professor S. Devi for their help and encouragement during this study. We wish to thank Mr. S. P. Sahoo of Sun Pharmaceutical Advanced Research Center and RSIC Chandigarh for recording some of the NMR spectra for this work.

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21. *General Procedure for the Heck reaction using (2-bromoethyl)benzene* ***3*** *as styrene source. Preparation of catalyst solution (in all the cases catalyst is separately prepared as follows):* In a typical procedure a catalyst solution was separately prepared in an oven dried, N_2 flushed two-necked r.b. flask. A solution of palladium acetate (1.2 mg, 0.0055 mmol, 0.5 mol %) and ligand **7** (2.6 mg, 0.0137 mmol, 1.25 mol %) was prepared in dry *N*,*N*-dimethylacetamide (5 mL), under N_2 atmosphere. The mixture was stirred at room temperature until

homogeneous (about 15 min) and degassed several times prior to use.

In another dry N_2 flushed two-necked round bottomed flask a mixture of iodobenzene **13** (0.2 g, 0.98 mmol), dry K_2CO_3 (0.406 g, 2.94 mmol) in dry *N*,*N*-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N_2 gas. Then the solution was heated to 60 °C and (2-bromoethyl)benzene **3** or (1-bromoethyl)benzene **4** (0.217 g, 1.17 mmol) was slowly added. Then the temperature was increased to 100 °C, previously prepared palladium catalyst solution was added dropwise, and the reaction mixture was heated to 140 ± 5 °C for 40 h. The cooled mixture was then poured into water (25 mL) containing 6 N HCl (5 mL) and extracted with dichloromethane (3 × 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to give *trans*-stilbene **14** as white solid (0.140 g, 80%) (Table 1, entry 1).

General Procedure for the one pot Wittig–Heck reaction: Catalyst solution was prepared in the same way as above. In another dry N_2 flushed two-necked r.b. flask a mixture of iodobenzene **13** (0.5 g, 2.45 mmol), benzaldehyde **5** (0.260 g, 2.45 mmol), triphenylmethylphosphonium iodide (0.995 g, 2.45 mmol), TBAB (0.158 g, 0.49 mmol), and K_2CO_3 (1.18 g, 8.57 mmol) in dry *N*,*N*-dimethylacetamide (5 mL) was taken and kept under N_2 atmosphere. The solution was then heated to 100 °C, previously prepared palladium catalyst solution was added dropwise, and the reaction mixture heated to 140 ± 5 °C for 40 h. The cooled mixture was then poured into water (25 mL)and extracted with dichloromethane (3 × 30 mL). The dry solution (Na_2SO_4) was concentrated and purified by column chromatography using silica gel and petroleum ether as eluent to give *trans*-stilbene **14** as white solid; mp 121–122 °C (0.401 g, 91%, entry 1 of Table 2)