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Sunlight promoted palladium catalysed Mizoroki–Heck, Suzuki–Miyaura and Sonogashira reactions

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ABSTRACT

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One of the twelve principles of 'Green Chemistry' proposed by Anastas and Warner refers to the use of energy efficient synthetic processes.¹ The sixth principle says 'the energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.' The solar energy is the greenest source of energy, it is abundant, cheaper and a cleaner alternative to any process of generation of energy. It is the most powerful form of renewable energy.

The use of solar energy to drive chemical transformations was recognized very early^{2,3} and many efforts are made to explore different reactions under the natural sunlight. The direct sunlight or concentrated sunlight is utilized either as a photon source for photochemical or photothermal reactions. Some of the sunlight induced reactions involve dimerization⁴ or *cis–trans* isomerization of alkenes and the conjugated compounds⁵ and the related reactions. Beside these a few other sunlight mediated reactions have been developed over the years and are summarized in recent articles.^{6,7} However, the focus of research has mostly been directed to the chemistry of molecules which are capable of absorbing light for the desired bond modifications leading to chemical changes.

The palladium catalysed coupling reactions are now well established tools of modern synthetic chemists. Mizoroki–Heck reaction to synthesize stilbenes or cinnamates,^{8,9} Suzuki–Miyaura reaction¹⁰ for biaryls or substituted alkenes and Sonogashira reaction¹¹ for the preparation of substituted alkynes are the three main reactions of this class. These reactions are traditionally carried out in the thermal conditions in the presence of catalysts and suitable additives. Use of microwave or ultrasound irradiation to drive these reactions has also been explored with varied success.¹² In this communication we present our efforts to perform these important reactions under the direct solar irradiation without the need of any special apparatus or conditions.

The intended driving force is the photothermal energy received from sunrays. Recently we have screened a series of $1-(\alpha-\text{aminobenzyl})-2$ -naphthols as phosphine free ligands for these three reactions with reasonably good conversions at conventional heating conditions¹³ (Fig. 1).

Initially, Mizoroki–Heck reaction of iodobenzene with styrene was investigated under the conditions presented in Scheme 1. The reaction was performed in a simple assembly of an Erlenmeyer flask fitted with a guard tube and a magnetic stirrer. The reaction was simply exposed to bright sunlight continuously for several days and then the product was isolated. For better results the flask



Figure 1. Ligands for the present study.







The palladium catalysed Mizoroki-Heck, Suzuki-Miyaura and Sonogashira reactions were successfully

carried out under irradiation with sunlight. The Heck reaction gives considerable amount of Z product

due to photochemical isomerization of initially formed *E* alkenes. Reaction of methyl 2-iodobenzoate

with acrylamide under solar condition furnished 2H-2-benzazepine-1,3-dione rather than the expected

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Scheme 1. Comparison of Mizoroki–Heck reaction under the solar irradiation performed in open or dark vessels.

is placed on top of a simple mirror to utilize the reflected sunrays. However, it was interesting to observe the formation of *Z*-stilbene (Z-1) as a major product compared to *E*-stilbene (E-1) contrary to the usual selectivity of the reaction (Eq. 1).

This could probably be due to the photochemical isomerization of stilbene like compounds when exposed to light.¹⁴ Another experiment was conducted under identical condition but the flask was completely covered with a black paper to prevent exposure to light (Eq. 2). This experiment gave exclusively trans-stilbene (E - 1) as earlier observed for the same catalyst system for the classical thermal conditions.^{13a} Identical results were obtained when iodobenzene was treated with acrylates to form Z/E cinnamates. Further evidence to the possibility that the initially formed *E* olefin was getting isomerized to *Z* olefin over a period of sunlight exposure was provided by a separate experiment. In this study the pure *E*-ethyl cinnamate was gradually converted into *Z* isomer till it reached the equilibrium or photostationary phase in about 56 h of actual sunlight (Fig. 2).

1 3 4

1 * 11 1

Table 1



Figure 2. Isomerization of ethyl cinnamate under sunlight irradiation (\blacksquare for *E* isomer; \blacktriangle for *Z* isomer).

We also observed a very poor conversion when the same reaction was performed at room temperature without exposure to the sunlight (9% Y) or with only Pd(OAc)₂ in sunlight in the absence of the ligand (18% Y). The reaction proceeds mainly due to the photothermal reaction as we have measured the reaction temperature to reach about 56–58 °C in the day time when the brightest sunlight falls on the reaction medium. However, the role of photochemical cleavage of Ar–I bond for the S_{RN}1 type substitution reaction assisted by sunlight cannot be ruled out.¹⁵ This also accounts for the observation of low reactivity of Ar–Br in this reaction under the solar conditions. The reduction of Pd(II) to Pd(0) can also be assisted under the photochemical conditions as postulated by Köhler.¹⁶ This is the only known report on the beneficial effect of artificial light on the Mizoroki–Heck reaction.

Having reasonably established the conditions of optimized conversion, a series of substrates were screened with moderate to

No	ArX	Alkene ^a	Product	Yield ^b /% [Z:E] ^c
1	C ₆ H ₅ l	COOEt	C ₆ H ₅ 2 COOEt	86 [25:75]
2	C ₆ H ₅ I	COO ^t Bu	C ₆ H ₅ 3	85 [19:81]
3	4-ClC ₆ H ₄ Br	COO ^t Bu	4-CIC ₆ H ₄ 4	41 [21:79]
4	4-RC ₆ H ₄ l	COOEt	$4-RC_6H_4$ 5 R = NHCOCH ₃	84 [55:45]
5	2-RC ₆ H ₄ I	COOEt	$2-RC_6H_4 \xrightarrow{\sim} COOEt$ 6 R = COOCH_3	69 [70:30]
6	2-RC ₆ H ₄ l	COO ^t Bu	2-RC ₆ H ₄ COO ^t Bu 7 R = COOMe	78 [78:22]
7	2-MeC ₆ H ₄ l	COOEt	2-MeC ₆ H ₄ 8	90 [80:20]
8	C ₆ H ₅ l	CONH ₂	C ₆ H ₅ 9 CONH ₂	76 [48:52]
9	2-RC ₆ H ₄ l	Ph	$2-RC_{6}H_{4} \xrightarrow{Ph}$ 10 R = COOEt	78 [69:31]
10	4-BrC ₆ H ₄ l	COOEt	4-BrC ₆ H ₄ COOEt	83 [43:57]

^a General conditions: L-1 (0.6%), Pd(OAc)2 (0.5%), Et₃ N (2.0 equiv) in DMA, sunlight, 9 d.

^b Isolated yield in %.

^c Determined by H NMR analysis.



CH2=CH-CONH2, sunlight, Pd(OAc)2 (0.5 %), L-1 (0.6 %), Et3N (2 eq.), DMA, 9 d

Scheme 2. Unexpected cyclization in Mizoroki-Heck reaction in solar condition.



Scheme 3. Probable route for the formation of 15

 Table 2

 Sunlight induced Suzuki–Miyaura and Sonogashira reactions^a

No]	Reagents	Product(s)	Yield ^b /%
1	C ₆ H ₅ l	C ₆ H ₅ B(OH) ₂	C ₆ H ₅ -C ₆ H ₅ 16	91
				88 ^c
2	C ₆ H ₅ l	2-MeC ₆ H ₄ B(OH) ₂	2-MeC ₆ H ₄ -C ₆ H ₅ 17	83
3	C ₆ H ₅ l	3-HOC ₆ H ₄ B(OH) ₂	3-HOC ₆ H ₄ -C ₆ H ₅ 18	82
4	C ₆ H ₅ l	3-HOCH ₂ C ₆ H ₄ B(OH) ₂	3-HOCH ₂ C ₆ H ₄ -C ₆ H ₅ 19	77
5	C ₆ H ₅ l	$4-CHOC_6H_4B(OH)_2$	4-CHOC ₆ H ₄ -C ₆ H ₅ 20	55
			4-CHOC ₆ H ₄ -4-CHOC ₆ H ₄ 21	47
6	4-MeOC ₆ H ₄ l	$C_6H_5B(OH)_2$	4-MeOC ₆ H ₄ -C ₆ H ₅ 22	53
7	C ₆ H ₅ l	C ₆ H ₅ C=CH	C ₆ H ₅ C=CC ₆ H ₅ 23	84 ^d
				39 ^e
8	4-NO ₂ C ₆ H ₄ l	C ₆ H ₅ C=CH	4-NO ₂ C ₆ H ₄ C=CC ₆ H ₅ 24	80 ^d
9	2-CO ₂ EtC ₆ H ₄ l	C ₆ H ₅ C=CH	$2-COOEtC_6H_4C \equiv CC_6H_5$ 25	74 ^d

 a General conditions for Suzuki reaction; L-2 (0.6%), Pd(OAc)_2 (0.5%) K_2CO_3 (2 equiv) Dioxane-H_2O (1:1), sunlight, 1 d. b Isolated yield in %. For Sonogashira reaction: L-2 (1.2%), Pd(OAc)_2 (1.0%), base

^b Isolated yield in %. For Sonogashira reaction: L-**2** (1.2%), Pd(OAc)₂ (1.0%), base (2.0 equiv), NMP, sunlight, 3 d.

^c The reaction conducted in dark vessel.

- d With K₂CO₃.
- e With Et₃N.

good results (Table 1). The stilbenes or cinnamic acid derivatives formed were found to have a considerable amount of the *Z* isomer in most of the cases. The methods available for the synthesis of *Z* alkenes include selective hydrogenation of corresponding alkynes,¹⁷ from aldehydes by modified Wittig reaction,¹⁸ Favorskii reaction,¹⁹ Negishi coupling,²⁰ aldol reaction,²¹ Peterson reaction,²² photoisomerization of *E* alkenes²³ etc. Special conditions for Mizoroki–Heck reaction for selective formation of *Z* alkene has also been developed by some groups²⁴ which involves the design of ligand or other parameters. The similar olefinic moiety with *Z* stereochemistry is present in some bioactive molecules discovered recently.²⁵ For practical application, this reaction was carried out on a multi gram scale of iodobenzene (10.2 g, 0.05 mol) and ethyl acrylate (0.075 mol) to afford the ethyl cinnamate **2** in high yield (90.5% Y, *Z:E* ratio of 25:75). Reaction of ethyl 2-iodobenzoate **12a** with acrylamide under the same conditions afforded desired compound **13** in similar manner, but notably the reaction of methyl 2-iodobenzoate **12b** furnished a cyclized product, 2*H*-2-benzazepine-1,3-dione **14** (Scheme 2).²⁶

The latter reaction when performed under thermal conditions however, furnished the expected product **15** exclusively as the *E* isomer (Scheme 3). This unexpected observation for the sunlight induced Mizoroki–Heck reaction could be explained by the initial isomerization of compound from *E*-**15** to *Z*-**15** followed by intramolecular cyclization. The less favourable cyclization on ethyl ester as compared to methyl ester may be the reason for this observation in the case of **12a** and **12b**. This hypothesis was confirmed when a pure sample of *E*-**15** was initially converted into *Z*-**15** when exposed to sunlight and later cyclized to *2H*-2-benzazepine-1,3dione **14**.

The present protocol of sunlight assisted coupling was further extended to other two important coupling reactions. Preliminary investigations for the Suzuki–Miyaura and Sonogashira reactions are encouraging and the results are summarized in Table 2. The outcome of the Suzuki–Miyaura reaction in the absence of light was same as in open vessel indicating the sunlight is merely acting as a heating source (Table 2, entry 1).

The outcome of all three reactions with either ligand is almost similar. $^{\rm 13}$

The present findings offer a simple way to utilize sunlight as a renewable energy source for palladium catalysed basic coupling reactions without the need for any special apparatus or reaction machinery.^{27–29}

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- 28. General procedure for the Heck reaction under photochemical irradiation. Ethyl (2methyl)cinnamate (**8**) (Table 1, entry 7): To an oven-dried Erlenmeyer flask equipped with a stirrer bar and guard tube was charged 2-iodotoluene (0.25 g, 1.147 mmol), triethyl amine (0.232 g, 2.293 mmol), palladium acetate (1.29 mg, 0.006 mmol) and L-1 (2.18 mg, 0.007 mmol) in DMA (10 mL). To this reaction mixture ethyl acrylate (0.172 g, 1.72 mmol) was added. The reaction mixture was exposed to sunlight for 9 days. After completion of the reaction, the mixture was quenched with water and extracted with ethyl acetate (3 \times 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel (hexane) to afford ethyl (2-methyl)cinnamate **8** as a pale yellow oil (0.195 g, 90%) (Table 1, entry 7).% Yield: 90, *Z:E* 80:20.

¹H NMR (CDCl₃, 400 MHz): δ 8.0–7.1 (m, 5H, which also contains one set of *trans* & *cis* olefinic protons), 6.38–6.34 & 6.04–6.01 & (2d, *J* = 16 Hz & *J* = 12 Hz, 1H, second set of *trans* & *cis* olefinic protons), 4.3–4.06 (2q, 2H, –CH₂ of –COOEt group of *trans* & *cis* isomer), 2.44 & 2.3 (2s, 3H, Ar-CH₃ of *trans* & *cis* isomer), 1.36–1.13 (2t, 3H, –CH₃ of –COOEt group of *trans* & *cis* isomer). MS (EI): M/Z, (%): 190 (M)⁺ (11), 175 (5), 145 (56), 144 (63), 117 (29), 116 (59), 115 (100), 91 (25).

MS (EI): M/Z, (%): 190 (M)* (11), 175 (5), 145 (56), 144 (63), 117 (29), 116 (59), 115 (100), 91 (25).

IR (Neat): 3062, 2981, 1722, 1633, 1602, 1530, 1485, 1459, 1407, 1384, 1312, 1275, 1185, 1162, 1098, 1032, 982, 950, 839, 760, 730, 598 $\rm cm^{-1}.$

29. On an average a day's sunlight is equivalent to about 8 h of bright effective exposure of solar rays. The results vary slightly with respect to the time of the year and better conversions are observed in summer months.