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Heck-type reaction of aryldiazonium silica sulfates

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Abstract Aryldiazonium silica sulfates were employed as new and efficient reagents for Heck-type arylation reactions with styrene and methyl acrylate. The reactions were carried out in an organic solvent, in the presence of $Pd(OAc)_2$ as precatalyst without use of base and free ligand. The *trans* isomers of desired products, methyl cinnamates and stilbenes, were obtained with full conversion. Use of a catalytic amount of $Pd(OAc)_2$ produced the corresponding products in short reaction times and excellent yields.

Keywords Catalyst · Arylation · Transition metals compounds · Silicates

Introduction

The palladium-catalyzed Heck coupling reaction of aryl halides and alkenes [1, 2] was first reported in the early 1970s and is still one of the most important C–C bond formation reactions in synthetic chemistry [3–7] and the

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Pharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology, 84156 Isfahan, Iran preparation of natural products [8–11], fine chemicals, and pharmaceuticals [12, 13].

The application of expensive electrophiles such as aryl iodides, bromides, or triflates is a drawback for this significant reaction. The interesting use of diazonium salts instead of halides or triflates has been preferred in the last decade [14–19] owing to the higher reactivity of diazoniums which produce a better leaving group (nitrogen) than halides or triflates [20, 21]. Moreover, the use of the more readily available aniline derivatives as the arenediazonium salt precursors has more economic benefits in comparison with their halide or triflate alternatives [22–26]. Also, these reactions can usually be carried out under milder conditions, shorter reaction times, and with higher yields than conventional Heck reactions without using a base and additional ligands [27, 28].

Because of the instability and explosive nature of diazonium salts, their reactions must be carried out in the same medium in which they are produced [29]. Therefore, extended investigations have been aimed at the synthesis of arenediazonium salts which are stable under dry conditions [30, 31]. The application of arenediazonium salts in Heck-type reactions is highly dependent on the nature of the diazonium counter-anions [32]. These properties are distinctive to aryl diazonium tetrafluoroborates [33], hexafluorophosphates [34–37], and arenediazonium *o*-benezenedisulfonimides [37, 38].

In following up our research on C–C coupling reactions using *ortho*-palladated complexes as precatalysts [39–41], we have employed various arenediazonium salts synthesized previously [42–44] as electrophiles with styrene and methyl acrylate as olefins in Heck-type coupling reactions. The stability of aryldiazonium salts, ArN_2^+ –OSO₃SiO₂, was investigated at room temperature (RT) and the products were characterized by ¹H NMR, ¹³C NMR, and IR.

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Scheme 1



Results and discussion

Table 1 Optimization of catalyst concentration

Synthesis of arenediazonium salts

The instability of diazonium salts has often limited their applications as intermediates in organic synthesis. Usually, these compounds are synthesized at around 10 °C and handled below 0 °C to avoid their decomposition. In previous work [42–44] different kinds of aromatic amines were rapidly converted to the corresponding diazonium salts under solvent-free conditions at RT using amine (1 mmol), silica sulfuric acid (0.7 g), and sodium nitrite (2 mmol) which were ground in with a pestle a mortar for a few minutes to obtain an homogeneous mixture. After that, a few drops of water were slowly added and the reaction mixture was ground for 10–15 min until the complete evolution of nitrous acid gas (generated via the reaction of excess nitrite under acidic conditions). The corresponding arenediazonium salts were prepared quantitatively.

Heck-type arylation of aryldiazonium silica sulfates

The application of arenediazonium salts on the coupling reactions with two different olefins in the presence of a catalytic amount of $Pd(OAc)_2$ without using a base or additional ligands at RT has been investigated (Scheme 1).

The synthesis of methyl cinnamate derivatives **4** was investigated because of their importance in the synthesis of a vast variety of agrochemicals, as antioxidants in plastics, and their use as starting materials in the synthesis of a great set of pharmaceuticals [45, 46].

In order to evaluate the solvent effects the $Pd(OAc)_2$ catalyzed coupling reactions of phenyldiazoium silica sulfate with methyl acrylate at RT were carried out in several organic solvents such as ethanol, tetrahydrofuran (THF), CH_2Cl_2 , CH_3CN , and toluene. Accordingly ethanol turned out to be the best solvent. A variety of catalyst concentrations were tested and 2.5 mol% gave the best results (Table 1).

The optimized reaction conditions were the use of ethanol as reaction medium and 2.5 mol% of $Pd(OAc)_2$ at RT. It is interesting to mention that the reaction under the stated conditions proceeded successfully in the absence of ligands, bases, and nitrogen atmosphere.



Catalyst/mol%	Time/min	Temperature	Conversion/%	
None	30	RT	0	
8	10	RT	100	
4	10	RT	100	
2.5	10	RT	100	
1	30	RT	50	

The aforementioned conditions were applied in the Heck-type reaction of a variety of aryldiazonium salts **3** with methyl acrylate. Both electron-withdrawing and electron-donating groups (independent of their position on the aromatic ring, whether *ortho* or *para*) led to the production of the desired coupling compounds in excellent yields (Table 2, entries 1–10).

All of the methyl cinnamate derivatives were obtained in *trans* configuration. Entries 9 and 10 of Table 2 confirm that the reactions produce high chemoselectivity, because in the presence of diazonium groups, bromo or chloro moieties remain unchanged.

Besides the Table 2 entries, 1-naphthyldiazonium silica sulfate was synthesized and treated by methyl acrylate under the same reaction conditions and the related coupling product was obtained in 65% yield after 1 h.

To further explore the scope of the reaction, the production of several stilbene derivatives **5** through Heck-type reactions of various arenediazonium salts and styrene was examined as well (Table 3, entries 1–10). These beneficial compounds are used as the key monomers for the synthesis of conjugated aromatic oligomers and polymers [47]. Interestingly, *trans*-stilbene, which is the preferred isomer for the fabrication of the conjugated polymers, was obtained via the described procedure.

The molar ratio of diazonium salts to styrene was 1:1.5 and the same molar amount of $Pd(OAc)_2$ was used as catalyst. The reactions were carried out in ethanol at RT

 Table 2 Heck-type reaction of aryldiazonium salts with methyl acrylate using Pd(OAc)₂ as catalyst



Entry	Product	Х	Y	Time/min	Yield/% ^a
1	4 a	Н	Н	10	88
2	4b	CH ₃	Н	15	84
3	4c	Н	CH_3	20	82
4	4d	CN	Н	15	85
5	4e	CH ₃ CO	Н	15	84
6	4f	Н	COPh	45	82
7	4g	NO_2	Н	15	92
8	4h	Н	NO_2	15	88
9	4i	Br	Н	15	91
10	4j	Cl	Н	15	87

Reaction conditions: aryldiazonium silica sulfate, 1 mmol; methyl acrylate, 1.5 mmol; catalyst Pd(OAc)₂, 0.025 mmol; RT

^a Isolated yield

 Table 3 Heck-type reaction of aryldiazonium salts with styrene using Pd(OAc)₂as catalyst



Reaction conditions: aryldiazonium silica sulfate, 1 mmol; methyl acrylate, 1.5 mmol; catalyst Pd(OAc)₂, 0.025 mmol; RT

^a Isolated yield

and the products with *trans* geometry were prepared. The conversions were 100% except for entry 8 which had a conversion of 90%.

Table 4 shows the results obtained from the Heck-type reactions using arenediazonium o-benzenedisulfonimides 1 [48], tetrafluoroborates 2 [20, 49, 50], and the reported aryldiazonium silica sulfates 3. The comparison of theses data confirms that the presented study has provided a relatively rapid manner to perform Heck-type reactions in high yields. Furthermore, the difficulties of the substrates containing nitro substitutions [51] are overcome completely (Table 2, entries 8, 9 and Table 3, entry 4).

Conclusion

We have used the previously synthesized aryldiazonium silica sulfates as efficient substrates for the C–C bond formation with methyl acrylate and styrene to form the corresponding *trans*-cinnamates and *trans*-stilbenes, respectively, using palladium catalyst at RT. The stated products were obtained in excellent yields using either electron-withdrawing or electron-donating substituents independent of their positions on the aromatic rings. Additionally, it is to be noted that arenediazonium salts involving bromide or chloride substituents on the aromatic ring showed high chemoselectivity in that essentially only the diazonium group reacted. Further investigations of the applications of these aryldiazonium silica sulfates as stable diazonium salts are ongoing in our laboratories.

Experimental

FT-IR spectra were recorded on a Jasco-680 spectrophotometer (Japan). NMR spectra were recorded in CDCl₃ solutions at RT on a Bruker 400 MHz spectrometer (TMS was used as an internal standard).

All reagents were purchased from Merck and Aldrich and used without further purification. Aryldiazonium silica sulfates were prepared according to the previous work [42– 44]. The products were characterized by comparison with authentic samples and by spectroscopic data (FT-IR, ¹H NMR, ¹³C NMR).

Heck-type reactions of aryldiazonium silica sulfate with methyl acrylate and styrene

To a solution of $Pd(OAc)_2$ (2.5 mol%, 0.0056 g, 0.025 mmol) and methyl acrylate or styrene (1.5 mmol) in 10 cm³ EtOH, aryldiazonium silica sulfate (1 mmol) was added with stirring in one portion and the reaction mixture was stirred at RT. A plentiful evolution of nitrogen took place. The reaction progress was monitored by TLC (hexane/EtOAc, 75:25). After completion of the reaction, the mixture was diluted with 10 cm³ EtOAc and filtered

Table 4 Comparison of aryldiazonium silica sulfate (3) in reaction of styrene or methyl acrylate at RT with other aryldiazonium salts (1, 2)

Ar-N ₂ ⁺	Ar	Olefin	Catalyst/mol%	Solvent	Time/min	Yield/%
1 [48]	4-Me-Ph	Styrene	1	EtOH	840 ^a	60
3	4-Me-Ph	Styrene	2.5	EtOH	75	93
2 [20]	Ph	Styrene	10	EtOH	255	97
2 [20]	2-Me-Ph	Styrene	5	EtOH	240	38
3	Ph	Styrene	2.5	EtOH	30	87
3	2-Me-Ph	Styrene	2.5	EtOH	80	85
2 [49]	Ph	Methyl acrylate	2	BmimPF ₆	180	76
2 [49]	4-Br-Ph	Methyl acrylate	2	BmimPF ₆	180	82
3	Ph	Methyl acrylate	2.5	EtOH	10	88
3	4-Br-Ph	Methyl acrylate	2.5	EtOH	15	91
2 [50]	2-Me-Ph	Styrene	2	THF	300	75
2 [50]	4-Br-Ph	Styrene	2	THF	240	91
3	2-Me-Ph	Styrene	2.5	EtOH	80	85
3	4-Br-Ph	Styrene	2.5	EtOH	90	90

^a At 70 °C

after vigorous stirring. The residue was washed with EtOAc $(3 \times 10 \text{ cm}^3)$ and the combined organic layer was washed with 20 cm³ H₂O and then dried over anhydrous CaCl₂. The solvent was evaporated under reduced pressure to provide the pure product. The ¹H NMR and ¹³C NMR spectra of known compounds were identical to those in the literature [20, 40, 48–50, 52, 53].

Methyl trans-3-(2-benzoylphenyl)propenoate

$(4f, C_{17}H_{14}O_3)$

¹H NMR (400 MHz, CDCl₃): $\delta = 7.80-7.82$ (m, Ph, -*CH*=CH–CO–, 3H), 7.74–7.77 (m, Ph, 1H), 7.59–7.63 (d, Ph, 1H), 7.53–7.56 (m, Ph, 1H), 7.44–7.49 (m, Ph, 4H), 6.39 (d, J = 16 Hz, 1H, -CH=CH–CO–), 3.74 (s, OCH₃, 3H) ppm; ¹³C NMR (400 MHz, CDCl₃): $\delta = 197.1$ (-CO–Ph), 166.8 (-CO–OMe), 142.0 (-CH=CH–CO–), 139.4, 137.3, 134.7, 134.6, 134.2, 133.9, 133.6, 131.0, 130.8, 130.4, 130.1, 129.2, 129.1, 128.6, 128.1, 127.3 (Ph), 120.5 (-CH=CH–CO–), 51.7 (OCH₃) ppm; IR (KBr): $\bar{\nu} = 3,051$ (=C–H), 2,952 (C–H), 1,726 (C=O), 1,587 (C=C) cm⁻¹; HRMS (ESI): calcd for (C₁₇H₁₄O₃+H)⁺ 267.0938, found 267.0941.

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References

- 1. Heck RF, Nolley JP (1972) J Org Chem 37:2320
- Mizoroki T, Mori K, Ozaki A (1971) Bull Chem Soc Jpn 44:581
 Djakovitch L, Wagner M, Hartung CG, Beller M, Koehler K (2004) J Mol Catal A 219:121
- Choudary BM, Madhi S, Chowdari NS, Kantam ML, Sreedhar B (2002) J Am Chem Soc 124:14127
- Fabrizi G, Goggiamani A, Sferrazza A, Cacchi S (2010) Angew Chem Int Ed 49:4067
- 6. Kim SJ, Oh SD, Lee S, Choi SH (2008) J Ind Eng Chem 14:449
- 7. Felpin FX, Nassar-Hardy L, Callonnec FL, Fouquet E (2011) Tetrahedron 67:2815
- 8. Gaudin JM (1991) Tetrahedron Lett 32:6113
- 9. Overman LE, Ricca DJ, Tran VD (1993) J Am Chem Soc 115:2042
- 10. Tietze LF, Buhr W (1995) Angew Chem Int Ed 34:1366
- 11. Ren G, Cui X, Yang E, Yang F, Wu Y (2010) Tetrahedron 66:4022
- 12. de Vries JG (2001) Can J Chem 79:1086
- 13. Shinkai I, King AO, Larsen RD (1994) Pure Appl Chem 66:1551
- 14. Priego J, Carretero JC (1999) Synlett 1603:1603-1605
- 15. Darses S, Pucheault M, Genet JP (2001) Eur J Org Chem 1121
- 16. Carpes MJS, Correia CRD (2002) Tetrahedron Lett 43:741
- 17. Andrus MB, Song C, Zhang J (2002) Org Lett 4:2079
- Roglans A, Pla-Quintana A, Moreno-Manas M (2006) Chem Rev 106:4622
- Felpin FX, Miqueu K, Sotiropoulos JM, Fouquet E, Ibarguren O, Laudien J (2010) Chem Eur J 16:5191
- Masllorens J, Maas MM, Quintana AP, Roglans A (2003) Org Lett 5:1559
- 21. Dai M, Liang B, Wang C, Chen J, Yang Z (2004) Org Lett 6:221

- 22. Markovic S, Petrovic ZD, Petrovic V (2009) Monatsh Chem 140:171
- 23. Selvakumar K, Zapf A, Spannenberg A, Beller M (2002) Chem Eur J 8:3901
- 24. Darses S, Michaud G, Genet JP (1999) Eur J Org Chem 1875
- 25. Weigelt M, Becher D, Ströhl D, Bruhn C, Poetsch E, Steinborn D (1998) Monatsh Chem 129:1329
- 26. Doyle MP, Bryker WJ (1979) J Org Chem 44:1572
- 27. Negishi E, Coperet C, Ma S, Liou SY, Liu F (1996) Chem Rev 96:365
- Grigg R, Longanathan V, Santhakumar V, Sridharan V, Teasdale A (1991) Tetrahedron Lett 32:687
- 29. Filimonov VD, Trusova M, Postnikov P, Krasnokutskaya EA, Lee YM, Hwang HY, Kim H, Chi KW (2008) Org Lett 10:3961
- Barbero M, Degani I, Fochi R, Perracino P (1998) PCT EP9801145 (CNR Italy); Chem Abstr 129:244942
- Barbero M, Crisma M, Degani I, Fochi R, Perracino P (1998) Synthesis 1171
- Sengupta S, Sadhukhan SK, Bhattacharyya S (1997) Tetrahedron 53:2213
- Cygler M, Przybylska M, Elofson RM (1982) Can J Chem 60:2852
- Godovikova TI, Rakitin OA, Khmelnitskii LI (1983) Russ Chem Rev 52:440
- 35. Zollinger H (1994) Diazo chemistry I. VCH, Weinheim, p 24
- 36. Galli C (1988) Chem Rev 88:765
- 37. Barbero M, Degani I, Dughera S, Fochi R (2004) Synthesis 2386
- Barbero M, Degani I, Dughero S, Fochi R (1999) J Org Chem 64:3448

- Hajipour AR, Karami K, Pirisedigh A (2009) Appl Organomet Chem 23:504
- 40. Hajipour AR, Karami K, Pirisedigh A, Ruoho AE (2009) J Organomet Chem 694:2548
- 41. Hajipour AR, Karami K, Pirisedigh A (2010) Appl Organomet Chem 24:454
- Zarei A, Hajipour AR, Khazdooz L, Aghaei H (2009) Tetrahedron Lett 50:4443
- 43. Zarei A, Hajipour AR, Khazdooz L (2009) Synthesis 941
- Zarei A, Hajipour AR, Khazdooz L, Mirjalili BF, Chermahini AN (2009) Dyes Pigm 81:240
- Isacoff H (1979) Kirk-Othmer encyclopedia of chemical technology, vol 7. Wiley-Interscience, New York, p 152
- Garbe D (1986) Ullmann's encyclopedia of industrial chemistry, vol 7, 5th edn. Wiley-VCH, Weinheim, p 99
- Kraft A, Grimsdale AC, Holmes AB (1998) Angew Chem Int Ed 37:402
- Artuso E, Barbero M, Degani I, Dugher S, Fochi R (2006) Tetrahedron 62:3146
- 49. Kabalka GW, Dong G, Venkataiah B (2004) Tetrahedron Lett 45:2775
- 50. Andrus MB, Song C, Zhang J (2002) Org Lett 4:2079
- 51. Hajipour AR, Zarei A, Ruoho AE (2006) Synth Commun 36:1039
- 52. Filimonov VD, Trusova M, Postnikov P, Krasnokutskaya EA, Lee YM, Hwang HY, Kim H, Chi KW (2008) Org Lett 10:3961
- 53. Bradley JC, Durst T (1995) Can J Chem 73:1660