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LETTERS

Stereoselective Palladium-catalyzed Coupling of 3,7-Bis(*N,N*-dimethylamino)-10*H*-Dibenz[*b,e*]iodinium Iodide with *α,β*-Unsaturated Carbonyl Compounds

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Abstract: A palladium-catalyzed and stereoselective Heck-type reaction between the iodine heterocycle, 3,7-bis(*N,N*-dimethylamino)-10*H*-dibenz[*b,e*]iodinium iodide and α,β-unsaturated carbonyl compounds wasaccomplished at mild temperature in good yields.

Palladium-catalyzed reactions of hypervalent iodine reagents, hypervalent iodonium salts and iodanes, with olefins and organometallics (such as organo-stannanes, organoboron compounds) are versatile methods for the formation of carbon-carbon bonds.[1-4] These coupling reactions are very useful for the syntheses of biaryls and stereodefined conjugated enynes, in particular upon unsymmetrical cases. These reactions also afford the additional advantages of being largely unaffected by the presence of water, tolerating a broad range of functionality and forming nontoxic byproducts.[5,6] Recently, our interest in syntheses and reactions of iodine heterocyclic compounds led us to explore the use of these compounds palladium-catalyzed coupling reactions. Herein, we report a novel palladium-catalyzed coupling between 3,7-bis(*N,N*-dimethylamino)-10*H*-dibenz[*b,e*]iodinium iodide(1) with *α,β*-unsaturated carbonyl compounds(**2**) at ambient temperature as shown in scheme **1**.

The 3,7-bis(*N,N*-dimethylamino)-10*H*-dibenz[*b,e*]iodinium iodide(**1**) was prepared by a literature method, the form of yellow crystals, m.p. 196°C(decomp.).[7]

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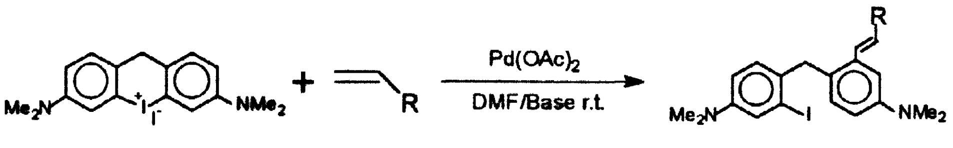


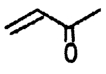
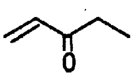
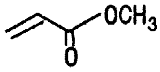
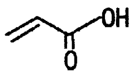
Scheme 1. R = CHO(**2a**), $COCH_3$(**2b**), COC_2H_5(**2c**), $COOCH_3$(**2d**), CN(**2e**), COOH(**2f**)

A typical procedure is as follows: To a mixture of iodine heterocycle (1mmol) and $Pd(OAc)_2$ (0.02mmol) in DMF(10ml) was added Na_2CO_3 (2mmol) and α,β-unsaturated compound (2mmol) in DMF(5ml) under argon. The mixture was stirred for 2-4hr at room temperature and quenched with 20ml of saturated NH_4Cl aqueous solution, and then extracted with diethyl ether (3×10ml). The ether layer was dried over anhydrous $MgSO_4$ and evaporated. The crude product was separated by flash chromatography on silica gel (Et_2O/petroleum ether = 1:2) to give product **3**.

The results summarized in Table 1 show that this coupling reaction gave coupling products **3** in satisfactory yields. The coupling reaction is similar to the related Heck reaction[8] and only trans-stereoselective products were obtained. This coupling reaction could proceed smoothly at room temperature as compared with that of Heck reaction. $Pd(OAc)_2$ was the best choice of catalyst in the coupling reaction. $PdCl_2$, $Pd(Ph_3P)_2Cl_2$ and Pd showed low catalytic activity and a very complex coupling mixture was obtained upon using $Pd(Ph_3P)_4$ as catalyst. Either organic or inorganic base was suitable for this reaction. When using Bu_3N, Na_2CO_3, and K_2CO_3, the reaction time was shortened and product yields were increased as compared with other bases. On the other hand, when NaOH, KOH, and NaOR were used in the coupling reaction as base, the iodine heterocycle decomposed. For the reaction of **1** and **2f**, using K_2CO_3 as base, the expected coupling product, **3f** was produced in 68% yield under similar conditions. Attempts to accomplish the coupling reaction of **1** with various α,β-unsaturated carbonyl compounds substituted further in the original group, such as methyl methacrylate and chalcone, were unsuccessful.

The coupling products (**3a-3f**) are, evidently, polyfunctionalized molecules, often to a variety of further transformations.

Table 1. Palladium-catalyzed Coupling of Iodine Heterocycle (1) with *α,β*-Unsaturated Carbonyl Compounds

Coupling product	α,β-Unsaturated compound		Reaction time (hr)	Isolated yield (%)
3a		**2a**	2	90
3b		**2b**	2	80
3c		**2c**	2.5	82
3d		**2d**	3	85
3e		**2e**	4	70
3f		**2f**	4	68

*The spectra and physical data of products are listed in the notes 9

References and Notes

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9. ***3a***: Yellow crystal, m.p.136-137 °C; M/Z 434(40), 264(40), 260(30) and 174(100); ^{1}H NMR ($CDCl_3$), δ (ppm): 2.91(s, 6H), 2.99(s, 6H), 4.03(s, 2H), 6.42(d, 1H, J=15.9Hz), 6.62-7.21(m, 6H), 7.83 (d, 1H, J=15.9Hz); IR(cm^{-1}) 3020, 1674,1596, 952 and 976. ***3b***: Yellow crystal, m.p.164-165 °C; M/Z 448 (100), 405(37), 277(28), and 188(75); ^{1}H NMR ($CDCl_3$), δ (ppm): 2.33(s, 3H), 2.91(s, 6H), 2.99(s, 6H), 4.04 (s, 2H), 6.55(d, 1H, J=16.1Hz), 6.61-7.23(m, 6H), 7.67(d, 1H, J=16.1Hz); IR(cm^{-1}) 3020, 1660, 1600, 953 and 975. ***3c***: Yellow crystal, m.p.124-125 °C; M/Z 462(65), 405(30), 390(17) and 277(22); ^{1}H NMR ($CDCl_3$), δ (ppm): 1.13(t, 3H,J=7.3Hz), 2.68(q, 2H, J=7.3Hz), 2.91(s, 6H), 2.99(s, 6H), 4.04(s, 2H), 6.48(d, 1H, J=15.9Hz), 6.62-7.24(m, 6H), 7.63(d, 1H, J=16.0Hz); IR(cm^{-1}) 3020, 1660, 1599, 950 and 980. ***3d***: Green needle crystal, m.p.131-132 °C; M/Z 464(100), 277(22) and 264(29); ^{1}H NMR ($CDCl_3$), δ (ppm): 2.91(s, 6H), 2.99(s, 6H), 3.61(s, 3H), 4.02(s, 2H), 6.35(d, 1H, J=15.6 Hz), 6.63-7.24(m, 6H), 7.97(d, 1H, J=15.6 Hz); IR(cm^{-1}) 3020, 1706, 1595, 946 and 975. ***3e***: Yellow-brown crystal, m.p.148-149 °C; M/Z 431(100), 304(12), and 289(10); ^{1}H NMR ($CDCl_3$), δ (ppm): 2.93(s, 6H), 2.99(s, 6H), 3.95(s, 2H), 5.77(d, 1H, J=16.5Hz), 6.62-7.25(m, 6H), 7.62(d, 1H, J=16.5Hz); IR(cm^{-1}) 3020, 2208, 1598 and 957. ***3f***: Green crystal, m.p.157-158 °C; M/Z 450(100), 277(30) and 264(55); ^{1}H NMR ($CDCl_3$), δ (ppm): 2.91(s, 6H), 2.99(s, 6H), 4.03(s, 2H), 6.42(d, 1H, J=15.9Hz), 6.62-7.21(m, 6H), 7.83(d, 1H, J=15.9Hz), 11.8(br, 1H); IR(cm^{-1}) 3020, 1678, 1599, 951 and 979.