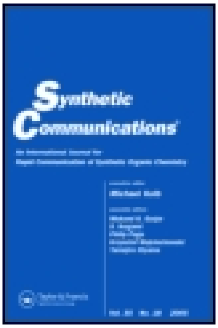

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Hypervalent Iodine in Synthesis XXX: Palladium-Catalyzed Reaction of Diaryliodonium Salts with β-substituted-α, β-enones

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Hypervalent Iodine in Synthesis XXX: Palladium-Catalyzed Reaction of Diaryliodonium Salts with β-substituted-α, β-enones

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Abstract: The reaction of diaryliodonium salts with β-substituted-α,β-enones in the presence of a palladium catalyst affords H_β–substituted products with excellent yields.

It is well known that olefinic systems react with σ-bonded carbon (sp^2)-palladium complexes to give unstable σ-alkylpalladium species which undergo a rapid and spontaneous *syn*-β-elimination of HPdX to form vinylic substitution products[1]. However, this reaction can not be effectively expanded to β-substituted -α, β-enones. Recently, Amorese and co-workers have reported that by controlling the added base, the palladium catalyzed reaction of α, β-enones with aryl halides can be dealt with to favor the formation of vinylic substituted products instead of conjugated addition products[2]. In most of their cases, however, the reactions needed high temperature and long reaction times. In our attempts to find an alternative to aryl halides for more satisfactory results and mild conditions, we focused our attention on hypervalent iodine compounds. We have investigated the palladium–catalyzed reaction of diaryliodonium salts with β-substituted-α,β-enones[3]. Here we reported our results.

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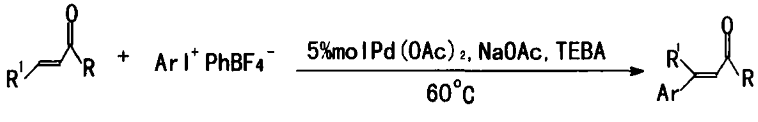
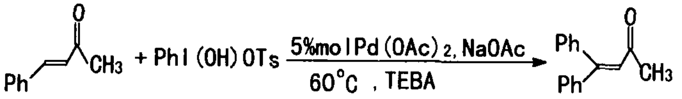
We found that excellent yields of H_β–substituted products could be obtained under mild conditions when β-monosubstituted α,β-enones reacted with diaryliodonium salts using 5mol% $Pd(OAc)_2$ as a catalyst and NaOAc as a base in the presence of TEBA. The results are summarized in Scheme 1 and Table 1.



(**Scheme 1**)

Our data indicate that substitutents attached to the aromatic ring of the diaryliodonium salts may facilitate or retard the reaction through their electronic effects. Diaryliodonium salts with electron-donating groups readily reacted with shorter reaction time and high yield. The reaction of diaryliodonium salt with electron–withdrawing group, such as Cl (entry 4), was slow. Diaryliodonium salt with strong electron–withdrawing group, such as NO_2- (entry 7), did not react even after very long reaction times. For unsymmetrical diaryliodonium salts (entry 5, 6), the reaction can be carried out smoothly to provide single products with the elimination of PhI. Besides, we found Koser's reagent, PhI(OH)OTs[14] also can be used in the reaction to afford the corresponding product. (Scheme 2)



83% yield

(**Scheme 2**)

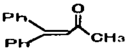
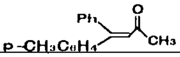
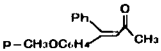
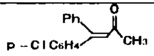
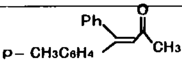
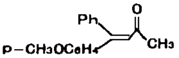
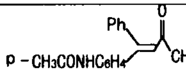
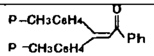
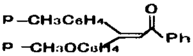
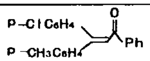
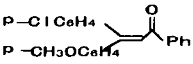
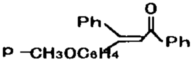
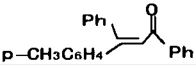
In summary, diaryliodonium salts react with β-substituted-α,β-enones in the presence of a palladium catalyst with excellent yield. We consider the process reported herein to be a valuable addition to Heck-type method because of its mild conditions, the wide range of structural types availed, and its ease of operation.

Experimental Section:

General procedure for the reaction of diaryliodonium salts with α,β-enones in the presence of $Pd(OAc)_2$:

Under N_2, the diaryliodonim salt or Koser's reagent (1.2mmol), TEBA (1mmol), NaOAc (2.5mmol) and 5mol% $Pd(OAc)_2$ were added to a stirred solution of α,β -enone (1mmol) in 10mL DMF . The mixture was stirred at 60°C until TLC indicated the disappearance of the starting material. The resulting mixture was quenched with saturated NH_4Cl solution (10mL), then

Table 1. Palladium-catalyzed reaction of β-monosubstituted α,β-enones with iodonium salts [a]

Entry	Iodonium Salt	Time(h)	Product	Yield(%)[b]
1	$Ph_2I^+BF_4^-$	6		81
2	$(p\text{-}CH_3C_6H_4)_2I^+BF_4^-$	6		84
3	$(p\text{-}CH_3OC_6H_4)_2I^+BF_4^-$	3		93
4	$(p\text{-}ClC_6H_4)_2I^+BF_4^-$	10		70
5	$p\text{-}CH_3C_6H_4I^+PhBF_4^-$	6		80
6	$p\text{-}CH_3OC_6H_4I^+PhBF_4^-$	3		87
7	$(m\text{-}O_2N\,C_6H_4)_2I^+BF_4^-$	20	———	———
8	$p\text{-}(CH_3CONHC_6H_4)_2I^+BF_4^-$	4		74
9	$(p\text{-}CH_3C_6H_4)_2I^+BF_4^-$	6		86
10	$(p\text{-}CH_3OC_6H_4)_2I^+BF_4^-$	3		96
11	$(p\text{-}CH_3C_6H_4)_2I^+BF_4^-$	6		82
12	$(p\text{-}CH_3OC_6H_4)_2I^+BF_4^-$	4		90
13	$(p\text{-}CH_3OC_6H_4)_2I^+BF_4^-$	3		89
14	$(p\text{-}CH_3C_6H_4)_2I^+BF_4$	6		80

a. The reaction was carried out with 1.2mmol iodonium salt, 1mmol α,β-enone, 1mmolTEBA, 2.5mmol Na_2CO_3 and 5%mmol $Pd(OAc)_2$ in 10mL DMF at 60° C for the time indicated; b. Isolated yield

extracted with ether (2x5mL). The combined organic layers were washed with water dried over anhydrous $MgSO_4$ and the solvent was evaporated. The crude product was isolated by SiO_2 column chromatography using petroleum ether/dichloromathane (4:1) as eluent to afford pure product.

Entry 1. oil (Lit.[5] oil) ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)= 2.11(s, 3H), 6.65(s, 1H), 7.10-7.53(m, 10H) I.R.(liquid film) ν (cm^{-1})=3030, 2980, 1650, 1600, 1570, 1480, 1440, 980, 930, 850, 830, 750, 720, 690 Analy. Caculd. for $C_{16}H_{14}O$ C 86.45, H 6.34; Found C 86.30, H 6.37

Entry 2 and 5. oil (Lit [6] oil) ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)=2.13(s, 3H), 2.38(s, 3H), 6.73(s,1H), 7.08-7.58(m,9H) I.R.(liquid film) ν (cm^{-1})=3060, 2960, 1660, 1610, 1570, 1480, 1440, 930, 850, 750, 720, 700 Analy. Caculd. for $C_{17}H_{16}O$ C 86.40, H 6.82; Found C 86.48, H 6.75

Entry 3 and 6. oil ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)=2.13(s, 3H), 3.84(s, 3H), 6.76(s, 1H), 6.96-7.63(m, 9H) I.R.(liquid film) ν (cm^{-1})=3060, 2960, 1660, 1600, 1570, 1480, 1440, 1250, 1130, 890, 830, 750, 690 MS m/z(%) 251(65), 237(100), 221(78), 178(35), 115(27), 105(13) Analy. Caculd. for its derivative of 2, 4-dinitrobenzenhydrazone $C_{23}H_{20}N_4O_5$ C 63.83, H 4.53; Found C 63.88, H 4.63

Entry 4. oil, (Lit. [6] oil) ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)= 2.13(s, 3H), 6.70(s, 1H), 7.13-7.58(m, 9H) I.R.(liquid film) ν (cm^{-1})=3070, 2980, 1660, 1605, 1570, 1470, 1430, 890, 820, 750, 730, 710, 690 Analy. Caculd. for $C_{16}H_{13}ClO$ C 74.85, H 5.10; Found C 74.92, H 5.06

Entry 8. M. P. 119-122°C (Lit. [7] 121-122°C) ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)=2.11(s, 3H), 2.20(s, 3H), 6.76(s, 1H), 7.10-7.78(m,9H), 8.37(s, 1H) I.R.(KBr) ν (cm^{-1})=3320, 3060, 2960, 1680, 1650, 1595,1575, 1480, 1430, 1180, 830, 770, 700

Entry 9. M.P. 113-115°C ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)=2.33(s, 3H), 2.37(s, 3H), 6.85-7.57(m, 14H) I.R.(KBr) ν (cm^{-1})=3060, 2980, 1665, 1610, 1585, 1480, 1440, 1070, 890, 850, 830, 750, 700 MS m/z(%) 312(100), 297(57), 282(49), 221(34), 207(29), 179(24), 145(21), 115(23), 105(18), 91(13), 77(20) Analy. Caculd. for $C_{23}H_{20}O$ C 56.34, H 6.23; Found C 56.41, H 6.41

Entry 10. M.P. 84-86°C ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)=2.37(s, 3H), 3.84(s, 3H), 6.83-7.87(m,14H) I.R.(KBr) ν (cm^{-1})=3030, 2980, 1665, 1610, 1580, 1480, 1440, 1260, 1130, 1100, 890, 850, 830, 750, 700 MS m/z(%) 327(100), 313(87), 297(54), 221(33), 207(28), 145(21), 115(18), 105(14), 77(10) Analy. Caculd. for $C_{23}H_{20}O_2$ C 53.58, H 5.91; Found C 53.66, H 6.10

Entry 11. M.P. 133-135°C ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)=2.37(s, 3H), 6.93-7.88(m, 14H) I.R.(KBr) ν (cm^{-1})=3030, 2970, 1650, 1600, 1580, 1480, 1440, 850, 835, 735, 710, 690 MS m/z(%) 332(100), 317(23), 165(31), 135(48), 105(37), 77(51) Analy. Caculd. for $C_{22}H_{17}ClO$ C 49.32, H 5.03; Found C 49.40, H 5.12

Entry 12. M.P. 121-122°C ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)=3.87(s, 3H), 6.84-7.93(m, 14H) I.R.(KBr) ν (cm^{-1})=3040, 2980, 1660, 1610, 1550, 1480, 1440, 1260, 1135, 1105, 850, 830, 735, 720, 700 MS m/z(%) 347(100), 333(21), 317(19), 271(17), 165(28), 135(23), 105(32), 77(56) Analy. Caculd. for $C_{22}H_{17}ClO_2$ C 47.07, H 4.63; Found C 47.13, H 4.77

Entry 13. M.P. 72-74°C (Lit. [8] 74-75°C) ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)=3.80(s, 3H), 6.87-7.58(m, 15H) I.R.(KBr) ν (cm^{-1})=3060, 2960, 1660, 1600, 1575, 1480, 1440, 1260, 1130, 1105, 850, 835, 735, 710, 690
Entry 14. M.P. 103-105°C (Lit. [8] 105-106°C) ^{1}H-NMR(60Hz, $CDCl_3$) δ (ppm)=2.37(s, 3H), 6.72-7.43(m, 15H) I.R.(KBr) ν (cm^{-1})=3075, 2980, 1660, 1600, 1580, 1560, 1480, 1440, 860, 820, 750, 730, 700

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