chance of being formed unless the approaching atom has a relatively large kinetic energy. This effect may play a more dominant role in $SiHCl_3$ than in SiH_2Cl_2, and is directly related to the polarizabilities of the bound atoms, e.g., polarizability of $H = 0.42 \times 10^{-24}$ and of $Cl = 2.28 \times 10^{-24}$ cm^3. Secondly, the variation in activation energy may be linked to the changes of electron density on the hydrogen atom, where the lower activation energy is associated with the H having the higher electron density. The polar effect may therefore be expected in the chloro-silanes involving the attack by the electrophilic Cl radical, where the inductive effect of Cl atoms should decrease the H electron density on the silanes with higher numbers of chlorine atoms. On the other hand, the inductive effect is offset to some extend by $d\pi$-$P\pi$ bonding which plays an important role in the case of the chlorine atom. This back-coordination reaches a maximum when three chlorine atoms are attached to silicon.[22] From the foregoing discussion, we suggest that the inductive effect gives a small contribution to di- and tri-chloro substitutions, leading to a similar electron density on the hydrogen atoms and thus to a slight difference in activation energies.

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Palladium Catalyzed Carbonylative Vinylation of Aryl Halides with Olefins and Carbon Monoxide

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The reaction of aryl iodides or bromides with olefins in the presence of 1 mol % of $PdCl_2(PPh_3)_2$ and 3 equiv. of n-Bu$_3$N at 100°C in carbon monoxide atmosphere gave the corresponding aryl vinyl ketones in good yields with small amount of vinylated 1-aryl olefins. But, when the reaction was proceeded under the 10 atm of carbon monoxide, aryl vinyl α-diketones and aryl vinyl ketones were obtained in moderate to good yields. The reaction was tolerant of a wide variety of functional groups on either the aryl halides or olefin compounds. Reactivity of aryl halide decrease in the order; aryl iodide > aryl bromide ≫ aryl chloride. In general, the reaction proceeded well and gave good yields of aryl vinyl ketones and aryl vinyl α-diketones when reactants are substituted with electron withdrawing groups.

Introduction

Aryl vinyl ketones[1,2] and aryl vinyl α-diketones[3-5] are im-

portant intermediates in the synthesis of a wide variety of organic compounds.

The palladium catalyzed aryl halide reaction with olefins

Table 1. Effect of Catalysts on the Carbonylative Vinylation of Bromobenzene with Styrene and CO[a]

(1)

(2)
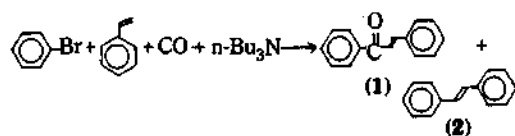
Entry	Catalyst	Reaction time, h	Products (% yield)[b] 1	2
1	Pd(OAc)$_2$ + P(o-tol)$_3$	24	0	0
2	Pd(OAc)$_2$ + PPh$_3$	24	0	0
3	Pd(OAc)$_2$ + P(n-Bu)$_3$	24	0	0
4	Pd(OAc)$_2$ + P(OPh)$_3$	24	trace	trace
5	Pd(OAc)$_2$ + P(OCH(CH$_3$)$_2$)$_3$	24	7	14
6	PdCl$_2$(PPh$_3$)$_2$	72	16	34
7	PdCl$_2$(CH$_3$CN)$_2$	72	14	28
8[c]	PdCl$_2$(PPh$_3$)$_2$	72	20	40

[a]General condition: 5 mmol of bromobenzene, 7 mmol of styrene, 15 mmol of n-Bu$_3$N, 0.05 mmol of Pd catalyst, and 0.1 mmol of phospine ligand at 100°C. p(CO) = atmosphere. [b]% Yield of isolated (% yield)[b] N (atm)

**Table 2.** Effect of Catalysts on the Carbonylative Vinylation of Iodobenzene with Styrene and CO[a]

(1)

(2)
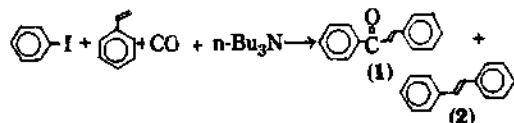
Entry	Catalyst	Products (%yield)[b] 1	2
1	Pd(OAc)$_2$	0	80
2	PdCl$_2$(PPh$_3$)$_2$	61	7
3	PdCl$_2$(CH$_3$CN)$_2$	50	9

[a]General condition: 5 mmol of iodobenzene, 7 mmol of styrene, 15 mmol of n-Bu$_3$N, and 0.05 mmol of Pd catalyst at 100°C for 24 h. p(CO) = atmosphere. [b]% Yield of isolated product.

provides a convenient method for the preparation of 1-aryl olefins[6,7]. The palladium catalyzed carboalkoxylation[8] and amidation[9-12] of aryl halides also have extensively been studied in past decades. Recently, Yamamoto *et. al.* reported the double carbonylation reaction of aryl halides with secondary amines catalyzed by palladium complexes to give α-keto amides[13].

In order to extend the scope of the palladium catalyzed reaction of aryl halides, we have investigated the reaction of aryl halides with olefins in the presence of carbon monoxide. In this study, we find that the reaction of aryl iodides or bromides with olefins and carbon monoxide in the presence of PdCl$_2$(PPh$_3$)$_2$ as a catalyst and n-Bu$_3$N at 100°C gives the corresponding aryl vinyl ketones and aryl vinyl α-diketones, resulting from vinylic substitution reaction accompanied by carbon monoxide insertion.

In the present paper, we report details of new and facile synthesis of aryl vinyl ketones and aryl vinyl α-diketones by the palladium catalyzed carbonylative vinylation of aryl

Table 3. Effect of CO pressure on the Carbonylative Vinylation of Iodobenzene with Styrene and CO[a]

(3)

(1)
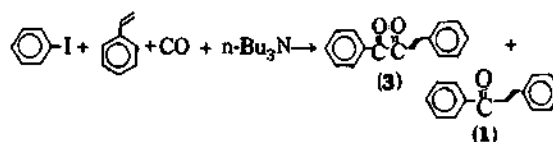
Entry	Catalyst	p(CO) (atm)	Products(% yield)[b] 3	1
1	PdCl$_2$(PPh$_3$)$_2$	1	10	60
2	PdCl$_2$(PPh$_3$)$_2$	2	35	38
3	PdCl$_2$(PPh$_3$)$_2$	4	45	22
4	PdCl$_2$(PPh$_3$)$_2$	10	50	20
5	PdCl$_2$(CH$_3$CN)$_2$	10	40	20
6	Pd(OAc)$_2$	10	40	15

[a]General condition: 5 mmol of iodobenzene, 7 mmol of styrene, 15 mmol of n-Bu$_3$N, and 0.05 mmol of Pd catalyst at 100°C for 24 h. [b]% Yield of isolated product.

halides.

Results and Discussion

Reaction Conditions. In order to find out optimum conditions for the mono and double carbonylative vinylation of aryl halides with olefins and CO, we examined the effects of substrate, catalyst and CO pressure.

First, the reaction of bromobenzene with styrene in a CO atmosphere at 100°C in the presence of 3 equiv. of n-Bu$_3$N and various palladium complexes as catalyst was studied. (Table 1). Reactions under usual vinylation catalyst systems[14] led to little to no reaction and fairly rapid deposition of a black solid, presumably palladium powder. (entries 1-5, Table 1). Employing dichlorobis(triphenylphosphine)palladium (II) (PdCl$_2$(PPh$_3$)$_2$) or dichlorobis(acetonitrile) palladium (II) (PdCl$_2$(CH$_3$CN)$_2$) as catalyst gave only low yields of carbonylatively vinylated (E)-1,3-diphenyl-1-oxo-2-propene(1) and moderate yields of vinylated (E)-stilbene(2). (entries 6-8, Table 1).

The reaction of iodobenzene with styrene in a CO atmosphere under the condition described above was also studied. (Table 2). Employing palladium acetate (Pd(OAc)$_2$) as catalyst gave only vinylated product 2 in 80% yield. (entry 1, Table 2). Whereas the reaction in the presence of PdCl$_2$(PPh$_3$)$_2$ catalyst was proceeded well and gave carbonylative vinylation product 1 in 61% yield along with 7% of 2 in 24 h. (entry 2, Table 2). Reaction under PdCl$_2$(CH$_3$CN)$_2$ catalyst also afforded 50% of 1 along with 9% of 2. (entry 3, Table 2).

On the other hand, chlorobenzene was so unreactive that it did not react even at 150°C.

In the reaction of iodobenzene with styrene and CO, higher CO pressures resulted in a double carbonylative vinylation. (Table 3). In the reaction under PdCl$_2$(PPh$_3$)$_2$ catalyst, the increase of the CO pressure enhances the double carbonylative vinylation and yields of (E)-1, 4-diphenyl-1, 2-dioxo-3-butene(3) were increased. (entries 1-4, Table 3). Thus, the reaction of iodobenzene with styrene under the 10 atm of CO at 100°C for 24 h in the presence of 1 mol% of PdCl$_2$(PPh$_3$)$_2$ and 3 equiv. of n-Bu$_3$N afforded 3 in 50% yield along with 20% of 1. (entry 4, Table 3). Reactions in the

Table 4. Mono Carbonylative Vinylation of Aryl Iodides with Olefins and CO[a]

Entry	Aryl Iodide	Olefin	Time,h	Products(% yield)[b] Mono Carbonylative Vinylated Product	Vinylated Product
1	Ph–I	styrene	24	PhCO–CH=CH–Ph (1) (61)	(7)
2	Ph–I	CH₂=CH–CO₂CH₃	24	PhCO–CH=CH–CO₂CH₃ (4) (67)	(5)
3	3-CH₃–C₆H₄–I	CH₂=CH–CO₂CH₃	20	(3-CH₃–C₆H₄)CO–CH=CH–CO₂CH₃ (5) (75)	(3)
4[c]	H₃CO–C₆H₄–I	CH₂=CH–CO₂CH₃	20	H₃CO–C₆H₄–CO–CH=CH–CO₂CH₃ (6) (82)	(3)
5[c]	O₂N–C₆H₄–I	CH₂=CH–CO₂CH₃	20	O₂N–C₆H₄–CO–CH=CH–CO₂CH₃ (7) (75)	(3)
6	HO–C₆H₄–I	CH₂=CH–CO₂CH₃	24	HO–C₆H₄–CO–CH=CH–CO₂CH₃ (8) (40)	(10)

[a] General condition: 5 mmol of aryl iodide, 7 mmol of olefin, 15 mmol of n-Bu₃N, and 0.05 mmol of PdCl₂(PPh₃)₂ at 100°C. p(CO)=atmosphere. [b] % Yield of isolated product. [c] DMF was used as solvent.

presence of Pd(OAc)₂ or PdCl₂(CH₃CN)₂ catalyst under the 10 atm of CO also gave 40% of 3 along with 15-20% of 1. (entries 5, 6, Table 3).
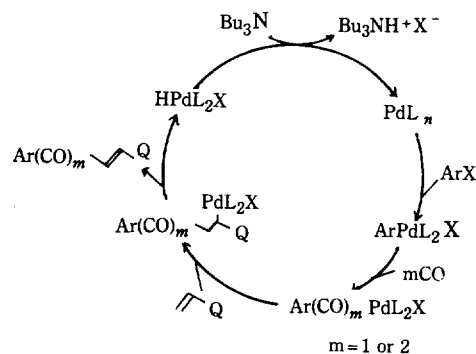
Mono and Double Carbonylative Vinylation of Aryl Iodides. On the basis of above results obtained, the standard condition employed for the mono carbonylative vinylation of aryl iodides with olefins and CO involved the use of 1 mol % of PdCl₂(PPh₃)₂ as catalyst and 3 equiv. of n-Bu₃N under the atmospheric pressure of CO at 100°C. (Table 4). As shown in Table 4, substituted aryl iodides were readily carbonylatively vinylated with methyl acrylate or styrene under the atmospheric pressure of CO and gave the corresponding aryl vinyl ketones in good yields along with small amount of vinylated 1-aryl olefins. The reaction of 4-iodoanisole with methyl acrylate under the condition described above gave 82% of (E)-methyl 4-(4-methoxyphenyl)-4-oxo-2-butenoate(6) along with 3% of vinylated product in 20 h. (entry 4, Table 4). Similarly, 3-iodotolune and 4-iodonitrobenzene were readily carbonylatively vinylated with methyl acrylate and gave good yields of the corresponding aryl vinyl ketones. (entries 3,5, Table 4). Whereas, the reaction of 4-iodophenol with methyl acrylate gave only 40% of (E)-methyl 4-(4-hydroxyphenyl)-4-oxo-2-butenoate(8) along with 10% of vinylated product. (entry 6, Table 4).

Substituted aryl iodides were reacted with methyl acrylate, styrene or acrylamide under the 10 atm of CO in the presence of 1 mol % of PdCl₂(PPh₃)₂ amd 3 equiv. of n-Bu₃N at 100°C for the syntheses of aryl vinyl α-diketones. Experimental results are summarized in Table 5. In general, substituted aryl iodides gave the corresponding aryl vinyl α-diketones in good yields along with 20-25% yields of aryl vinyl ketones. (entries 3-7, Table 5). However, reaction of 4-iodophenol with methyl acrylate gave only 35% of (E)-methyl

5-(4-hydroxyphenyl)-4, 5-dioxo-2-pentenoate(17) along with 20% of 8 in 48h. (entry 8, Table 5).

The mechanism of the present carbonylative vinylation of aryl halides with olefins and CO is not yet clear, but probably involves (a) oxidative addition of aryl halide to a Pd(0) species formed *in situ* from catalyst precursors such as PdCl₂L₂ to give arylpalladium halide, (b) CO insertion into the Pd-C bond in the arylpalladium intermediate to give aroyl or arylglyoxylpalladium species, (c) addition of aroyl or arylglyoxylpalladium intermediate to the olefinic double bond, and (d) internal elimination of a hydridopalladium halide group. (Scheme 1).

In conclusion, a new synthetic method has been developed for the preparation of aryl vinyl ketones and aryl vinyl α-diketones. The palladium catalyzed carbonylative vinylation of aryl halides with olefins and CO in the presence of n-Bu₃N gives aryl vinyl ketones or aryl vinyl α-diketones selectively depending on the CO pressure employed. The

m = 1 or 2

Scheme 1

Table 5. Double Carbonylative Vinylation of Aryl Iodides with Olefins and CO^a

Entry	Aryl Iodide	Olefin	Time,h	Products(% yield)^b Double Carbonylative Vinylated Product		Mono Carbonylative Vinylated Product
1	C$_6$H$_5$–I	styrene	24	C$_6$H$_5$–CO–CO–CH=CH–C$_6$H$_5$ **(3)**	(50)	**1**(20)
2	C$_6$H$_5$–I	∕∖CO$_2$CH$_3$	24	C$_6$H$_5$–CO–CO–CH=CH–CO$_2$CH$_3$ **(9)**	(53)	**4**(22)
3	(3-methylphenyl)–I	∕∕CO$_2$CH$_3$	24	(3-methylphenyl)–CO–CO–CH=CH–CO$_2$CH$_3$ **(10)**	(55)	**5**(22)
4^c	H$_3$CO–C$_6$H$_4$–I	∕∕CO$_2$CH$_3$	24	H$_3$CO–C$_6$H$_4$–CO–CO–CH=CH–CO$_2$CH$_3$ **(11)**	(60)	**6**(25)
5^c	H$_3$CO–C$_6$H$_4$–I	∕∕CONH$_2$	24	H$_3$CO–C$_6$H$_4$–CO–CO–CH=CH–CONH$_2$ **(12)**	(50)	H$_3$CO–C$_6$H$_4$–CO–CH=CH–CONH$_2$ **(13)** (20)
6^c	H$_3$CO–C$_6$H$_4$–I	styrene	24	H$_3$CO–C$_6$H$_4$–CO–CO–CH=CH–C$_6$H$_5$ **(14)**	(55)	H$_3$CO–C$_6$H$_4$–CO–CH=CH–C$_6$H$_5$ **(15)** (20)
7^c	O$_2$N–C$_6$H$_4$–I	∕∕CO$_2$CH$_3$	24	O$_2$N–C$_6$H$_4$–CO–CO–CH=CH–CO$_2$CH$_3$ **(16)**	(55)	**7**(22)
8	HO–C$_6$H$_4$–I	∕∕CO$_2$CH$_3$	48	HO–C$_6$H$_4$–CO–CO–CH=CH–CO$_2$CH$_3$ **(17)**	(35)	**8**(20)

^{a} General condition: 5 mmol of aryl iodide, 7 mmol of olefin, 15 mmol of n-Bu$_3$N, and 0.05 mmol of PdCl$_2$(PPh$_3$)$_2$ at 100°C. p(CO) = 10 atm. ^{b}% Yield of isolated product. ^{c} DMF was used as solvent.

gentle nature of the reaction allows many functional groups to be tolerated, including ester, amide, methoxy, nitro and hydroxy group.

Experimental

The ^{1}H NMR spectra were measured with a Varian Model S-60T spectrometer. Chemical shifts are given in δ units relative to tetramethylsilane as an internal standard. Infrared spectra were recorded on a Nicolet 5-DX FTIR spectrophotometer and the frequences are given in reciprocal centimeters. Mass spectra were recorded on a HP 5985-B mass spectrometer. Melting points were determined on a Fisher-Johns electrothermal melting point apparatus without correction. Gas chromatographic analyses were carried out on a Perkin Elmer Model Sigma-3B using 10% SE 30/Chromosorb W NAW, 2 m×1/4 in. column and helium as a carrier gas. Analytical thin layer chromatography was performed on precoated silica gel plates (0.2 mm, 60F$_{254}$, E. Merck) and silica gel (Kieselgel 60, 70-230 mesh, E. Merck) was used for column chromatography.

The aryl halides and olefins were commercial products. Dichlorobis(triphenylphosphine)palladium (II) (PdCl$_2$ (PPh$_3$)$_2$)[15] and dichlorobis (acetonitrile) palladium (II) (PdCl$_2$ (CH$_3$CN$_2$)[16] were prepared according to the literature methods.

General Procedure for the Preparation of Aryl Vinyl Ketones.

The following procedure for the preparation of (E)-1, 3-diphenyl-1-oxo-2-propene(1) is representative.

In a dry 100 ml flask equipped with a magnetic bar were placed 1.02g (5 mmol) of iodobenzene, 0.73g (7 mmol) of styrene, 2.78g (15 mmol) of n-Bu$_3$N and 0.04g (0.05 mmol) of PdCl$_2$(PPh$_3$)$_2$. After purging with CO gas for several times, the reaction flask was connected to a balloon filled with CO gas and stirred at 100°C for 24 h. At this time GLC analysis showed the absence of starting iodobenzene. The reaction mixture was cooled and stirred with ether and 10% aqueous hydrochloric acid. The organic layer was washed with 10% aqueous hydrochloric acid and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was seperated by column chromatography (hexane/ethyl acetate = 9/1(v/v)). 0.63g (61%) of (E)-1, 3-diphenyl-1-oxo-2-propene(1) and 0.06g (7%) of (E)-stilbene(2) were obtained.

(E)-1, 3-Diphenyl-1-oxo-2-propene(1)[17]: ^{1}H NMR(CDCl$_3$) δ 7.31-7.82(m, 10H), 7.92-8.18(m, 2H); IR(KBr) 1670 cm^{-1}; mp. 59°C; MS, m/e (M$^+$) calcd for C$_{15}$H$_{12}$O 208. 2592, found 208.2590.

Spectral Data of Aryl Vinyl Ketones.

(E)-Methyl 4-phenyl-4-oxo-2-butenoate(4): ^{1}H NMR (CDCl$_3$) δ 3.68(s, 3H), 7.19-7.68(m, 5H), 7.88-8.18(m, 2H); IR(neat) 1728, 1687 cm^{-1}.

(E)-Methyl 4-(3-methylphenyl)-4-oxo-2-butenoate(5): ^{1}H

NMR(CDCl$_3$) δ 2.38(s, 3H), 3.62(s, 3H), 7.02-7.49(m, 3H), 7.58-8.03(m, 3H); IR(neat) 1733, 1687 cm^{-1}.

(E)-Methyl 4-(4-methoxyphenyl)-4-oxo-2-butenoate(6): ^{1}H NMR(CDCl$_3$) δ 3.78(s, 3H), 3.92(s, 3H), 6.82(d, J = 8Hz, 3H), 7.30(d, J = 8Hz, 3H); IR(neat) 1737, 1676 cm^{-1}.

(E)-Methyl 4-(4-nitrophenyl)-4-oxo-2-butenoate(7): ^{1}H NMR (CDCl$_3$) δ 3.65(s, 3H), 7.62(d, J = 8Hz, 2H), 7.94-8.48 (m, 4H); IR(KBr) 1731, 1692 cm^{-1}.

(E)-Methyl 4-(4-hydroxyphenyl)-4-oxo-2-butenoate(8): ^{1}H NMR (DMSO-d$_6$) δ 3.62(s, 3H), 6.18(s, 1H), 6.92(d, J = 8Hz, 3H), 7.98(d, J = 8Hz, 3H); IR(KBr) 1737, 1703 cm^{-1}; mp. 179-180°C.

(E)-4-(4-Methoxyphenyl)-4-oxo-2-butenamide(13): ^{1}H NMR (CDCl$_3$) δ 3.82(s, 3H), 6.78-7.12(m, 3H), 6.92-7.12(bs, 2H), 7.72-8.28(m, 3H); IR(KBr) 1685, 1650 cm^{-1}; mp. 87°C.

(E)-1-(4-Methoxyphenyl)-3-phenyl-1-oxo-2-propene(15)[17]: ^{1}H NMR(CDCl$_3$) δ 3.78(s, 3H), 6.90(d, J = 8Hz, 2H), 7.20-7.67(m, 9H); IR(KBr) 1660 cm^{-1}; mp. 109-110°C.

General Procedure for the Preparation of Aryl Vinyl α-Diketones. The following procedure for the preparation of (E)-1,4-diphenyl-1,2-dioxo-3-butene(3) is representative.

1.02g (5 mmol) of iodobenzene, 0.73g (7 mmol) of styrene and 2.78g (15 mmol) of n-Bu$_3$N were added to a 100 m*l* stainless-steel pressure bottle containing 0.04g (0.05 mmol) of PdCl$_2$(PPh$_3$)$_2$ under nitrogen atmosphere. The bottle was pressurized to 10 atm with CO gas, and the pressure was released. This was repeated two more times, and the bottle was repressurized to 10 atm at room temperature. Then the mixture was magnetically stirred at 100°C for 24 h. After the CO gas was purged, the reaction mixture was stirred with ether and 10% aqueous hydrochloric acid. The organic layer was washed with 10% aqueous hydrochloric acid and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was seperated by column chromatography (hexane/ethyl acetate = 5/1 (v/v)). 0.71g (60%) of (E)-1, 4-diphenyl-1, 2-dioxo-3-butene(3) and 0.10g (10%) of **1** were obtained.

(E)-1, 4-Diphenyl-1, 2-dioxo-3-butene(3): ^{1}H NMR(CDCl$_3$) δ 7.28-7.81(m, 9H), 8.22-8.38(m, 3H); IR(neat) 1788, 1726 cm^{-1}; MS, m/e(M$^+$) calcd for C$_{16}$H$_{12}$O$_2$ 236.2696, found 236.2695.

Spectral Data of Aryl Vinyl α-Diketones.

(E)-Methyl 5-phenyl-4, 5-dioxo-2-pentenoate(9): ^{1}H NMR (CDCl$_3$) δ 3.71(s, 3H), 7.21-7.69(m, 5H), 8.02-8.38(m, 2H); IR (neat) 1785, 1725, 1693 cm^{-1}.

(E)-Methyl 5-(3-methylphenyl)-4, 5-dioxo-2-pentenoate (10): ^{1}H NMR(CDCl$_3$) δ 2.37(s, 3H), 3.62(s, 3H), 7.22-7.59 (m, 3H), 7.78-8.12(m, 3H); IR(neat) 1786, 1725, 1693 cm^{-1}.

(E)-Methyl 5-(4-methoxyphenyl)-4,5-dioxo-2-pentenoate (11): ^{1}H NMR(CDCl$_3$) δ 3.62(s, 3H), 3.93(s, 3H), 7.02(d, J = 8Hz, 3H), 8.14(d, J = 8Hz, 3H); IR(KBr 1787, 1719, 1688 cm^{-1}; mp. 83-84°C.

(E)-5-(4-Methoxyphenyl)-4-5-dioxo-2-pentenamide(12):

^{1}H NMR(CDCl$_3$) δ 3.90(s, 3H), 7.02(d, J = 8Hz, 3H), 6.91-7.21(bs, 2H), 8.18(d, J = 8Hz, 3H): IR(KBr) 1790, 1713, 1681 cm^{-1}; mp. 138-139°C.

(E)-1-(4-Methoxyphenyl)-4-phenyl-1,2-dioxo-3-butene(14): ^{1}H NMR(DMSO-d$_6$) δ 3.89(s, 3H), 6.91(d, J = 8Hz, 2H), 7.24-7.96(m, 9H); IR(KBr) 1778, 1718 cm^{-1}; mp. 69°C.

(E)-Methyl 5-(4-nitrophenyl)-4,5-dioxo-2-pentenoate(16): ^{1}H NMR(CDCl$_3$) δ 3.62(s, 3H), 7.33(d, J = 8Hz, 2H), 8.12-8.50(m, 4H); IR(KBr) 1785, 1715, 1687 cm^{-1}.

(E)-Methyl 5-(4-hydroxyphenyl)-4,5-dioxo-2-pentenoate (17): ^{1}H NMR(DMSO-d$_6$) δ 3.62(s, 3H), 6.21(s, 1H), 6.91(d, J = 8Hz, 3H), 8.27(d, J = 8Hz, 3H); IR(KBr) 1787, 1715, 1697 cm^{-1}.

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