

Synthesis of Diaryl α -Diketones via Palladium Catalyzed Double Carbonylative Homo Coupling of Aryl Iodides with Carbon Monoxide

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Symmetrical diaryl α -diketones were synthesized in moderately good yields through the palladium catalyzed reaction of aryl iodides with carbon monoxide. The reaction was tolerant of a wide variety of functionalities (OCH₃, CH₃, NO₂, OH, COOH) on the aryl iodide. On the other hand, the similar reaction of aryl bromides or chlorides with carbon monoxide did not proceed.

Introduction

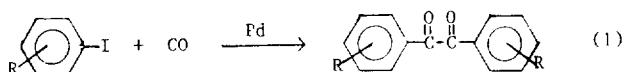
Symmetrical and unsymmetrical α -diketones are important precursors in the synthesis of a wide variety of organic compounds¹⁻⁴.

There are various methods^{1,5} available for the syntheses of α -diketones. The oxidation of α -methylene carbonyl compounds by selenium dioxide¹ is a good general route to α -diketones. α -Diketones are also accessible by the oxidation of acylolins¹, acetylenic compounds^{1,5b} and α -bromoketones^{5d}. Recently, Verlhac *et al.* reported the palladium catalyzed cross coupling of acyltins with acyl halides to give α -diketones⁶.

The homo coupling of aliphatic and aromatic halides to form dimers had been accomplished with various metals⁷ including palladium⁸. In connection with our study on the extension of the scope of the palladium catalyzed reaction of aryl halides⁹, we became interested in the carbonylative homo coupling of aryl halides with CO. In this paper, we wish to report a new synthesis of symmetrical diaryl α -diketones by the palladium catalyzed double carbonylative homo coupling of aryl iodides with CO.

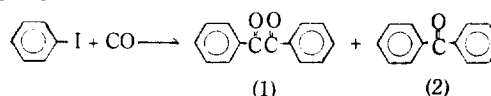
Results and Discussion

The palladium catalyzed reaction of aryl iodides with CO in the presence of an amine gave the symmetrical diaryl α -diketones in moderate to good yields (eq. 1).



In order to find out the optimum conditions for this double carbonylative homo coupling of aryl iodides with CO, we examined the effects of catalyst, solvent, reaction temperature and CO pressure on the reaction of iodobenzene with CO as a model reaction (Table 1). The reaction of iodobenzene with 10 atm of CO in the presence of 2 mol % of dichlorobis (triphenylphosphine)palladium(II) (PdCl₂(PPh₃)₂) and 3 equiv. of Et₃N at 100°C for 48 h gave benzil (**1**) only in 23% yield (entry 6, Table 1). However, addition of DMF to the reaction mixture afforded **1** in 57% yield with a trace amount of mono carbonylative homo coupled product, benzophenone (**2**), in 24 h

Table 1. Condition Study: Double Carbonylative Homo Coupling of Iodobenzene with CO^a


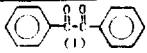

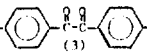

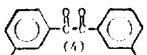

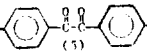

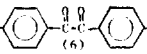

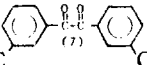


Entry	Catalyst	Solvent	Temp (°C)	Time (hr)	Product (% Yield) ^b	
					1	2
1	Pd(OAc) ₂	DMF	100	24	trace	trace
2	PdCl ₂ (PPh ₃) ₂	DMF	100	24	57	trace
3	PdCl ₂ (CH ₃ CN) ₂	DMF	100	24	45	0
4	Pd(PPh ₃) ₄	Benzene	100	32	34	0
5	Pd(PPh ₃) ₄	Toluene	100	36	30	0
6	PdCl ₂ (PPh ₃) ₂	none	100	50	23	0
7	PdCl ₂ (PPh ₃) ₂	Benzene	100	24	25	trace
8	PdCl ₂ (PPh ₃) ₂	CH ₃ CN	100	24	45	trace
9 ^c	PdCl ₂ (PPh ₃) ₂	DMF	100	24	57	trace
10 ^d	Pd(PPh ₃) ₄	Benzene	100	32	54	0
11 ^e	PdCl ₂ (PPh ₃) ₂	DMF	100	24	47	trace
12	PdCl ₂ (PPh ₃) ₂	DMF	r.t.	24	0	0
13	PdCl ₂ (PPh ₃) ₂	DMF	50	24	0	0
14	PdCl ₂ (PPh ₃) ₂	DMF	150	24	33	trace
15 ^f	PdCl ₂ (PPh ₃) ₂	DMF	100	24	56	trace

^aGeneral condition: 5 mmol of iodobenzene, 15 mmol of Et₃N, 5 ml of solvent, 0.1 mmol of catalyst, and 10 atm of CO. ^b% Yield of isolated product. ^c10 ml of DMF was used. ^d15 mmol of K₂CO₃ was used. ^eReacted under atmospheric pressure of CO. ^f0.25 mmol of PdCl₂(PPh₃)₂ was used.

(entry 2, Table 1). Employing palladium(II) acetate, dichlorobis(acetonitrile)palladium(II) (PdCl₂(CH₃CN)₂) or tetrakis (triphenylphosphine)palladium(0) (Pd(PPh₃)₄) instead of PdCl₂(PPh₃)₂ gave a lower yield of **2** (entries 1, 3, 4, Table 1). Increased amount of solvent and catalyst had no effect on the yield of **1** (entries 9, 15, Table 1). Also, the effect of solvent on the yield of **1** was studied (entries 2, 6-8, Table 1). DMF produced a higher yield of **1** than acetonitrile or benzene. The reaction at room temperature or 50°C was not proceeded and the starting iodobenzene was recovered (**2**) (entries 12, 13, Table 1). On

Table 2. Double Carbonylative Homo Coupling of Aryl Iodides with CO^a

Entry	Aryl Iodide	Time(hr)	Product(% Yield) ^b
1	 -I	2 4	 (57)
2	H ₃ CO-  -I	2 4	H ₃ CO-  -OCH ₃ (61)
3	 -I	2 4	 (55)
4	O ₂ N-  -I	2 4	O ₂ N-  -NO ₂ (60)
5	HO-  -I	4 8	HO-  -OH (40)
6	 -I	2 4	 (55)

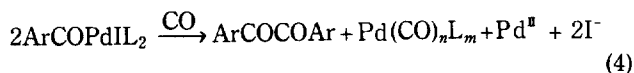
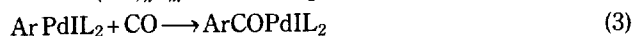
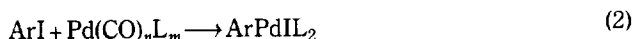
^aGeneral condition: 5 mmol of aryl iodide, 15 mmol of Et₃N, 5 ml of DMF, 0.1 mmol of PdCl₂(PPh₃)₂, and 10 atm of CO. ^b% Yield of isolated product.

the other hand, the reaction at 150°C gave a lower yield of **1** than at 100°C (entry 14, Table 1). Finally, the reaction under the atmospheric pressure of CO also proceeded well and gave a 47% yield of **1** (entry 11, Table 1).

On the basis of the above results, several substituted aryl iodides were reacted with CO. Experimental results are summarized in Table 2. As shown in Table 2, substituted aryl iodides were readily double carbonylative homo coupled with CO and gave the corresponding symmetrical diaryl α -diketones in moderately good yields. In general, electron-donating or electron-withdrawing substituents on the aryl iodide have no effect on the carbonylative homo coupling. However, a p-hydroxy substituent causes a significant reduction in the yield of α -diketone (entry 5, Table 2).

On the other hand, the similar reaction of bromobenzene or chlorobenzene with CO did not proceed and the starting material was recovered.

The mechanism of the present double carbonylative homo coupling of aryl iodide with CO is not yet clear, but probably involves (a) oxidative addition of aryl iodide to a Pd(0) species formed *in situ* from catalyst precursors such as PdCl₂L₂ to give arylpalladium iodide, (b) insertion of CO into the Pd-C bond in the arylpalladium iodide to give acylpalladium iodide, and (c) coupling of two acylpalladium iodide (eq. 2-4).



Experimental

The ¹H NMR spectra were measured with a Varian Model S-60T spectrometer. Chemical shifts are given in units relative to tetramethylsilane as an internal standard. ¹³C NMR spectra were obtained on a Bruker AM-200SY spectrometer. Infrared spectra were recorded on a Nicolet 5-DX FTIR spectrophotometer and the frequencies are given in reciprocal centimeters. Melting points were determined on Fisher-Johns electrothermal melting point apparatus

without correction. Analytical thin layer chromatography was performed on precoated silica gel plates (0.2 mm, 60F₂₅₄, E. Merck) and silica gel (Kieselgel 60, 70-230 mesh, E. Merck) was used for column chromatography.

The aryl iodides were commercial products. Dichlorobis(triphenylphosphine) palladium(II) (PdCl₂(PPh₃)₂)¹⁰, dichlorobis(acetonitrile) palladium(II) (PdCl₂(CH₃CN)₂)¹¹ and tetrakis(triphenylphosphine) palladium(0) (Pd(PPh₃)₄)¹² were prepared according to the literature methods.

General Procedure for the Preparation of Symmetrical Diaryl α -Diketones. The following procedure for the preparation of 4,4'-dimethoxybenzil (**3**) is representative.

1.17g(5 mmol) of 4-iodoanisole, 1.52g(15 mmol) of Et₃N and 5ml of DMF were added to a 100ml stainless-steel pressure bottle containing a magnetic stirring bar and 0.08g(0.1 mmol) of PdCl₂(PPh₃)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 stirred at 100°C for 24 h. After the CO gas was purged, the reaction mixture stirred with ether and 10% aqueous hydrochloric acid, and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was separated by column chromatography (hexane/ethyl acetate = 1/1(v/v)). 0.82g(61%) of 4,4'-dimethoxybenzil (**4**) was obtained. ¹H NMR (CDCl₃) δ 6.91 (d, J=8Hz, 4H), 7.98 (d, J=8Hz, 4H); IR(KBr) 1679 cm⁻¹; ¹³C NMR(CDCl₃) δ 54.72, 112.86, 122.50, 131.86, 162.52, 167.54; mp. 133-135°C (lit.¹³ 132-134°C).

Spectral Data of Symmetrical Diaryl α -Diketones.

Benzil(**1**): ¹H NMR(CDCl₃) δ 6.92-7.61 (m, 6H), 7.65-8.12 (m, 4H); IR(KBr) 1680 cm⁻¹; mp. 94-95°C (lit.¹⁴ 94-95°C).

3,3'-Dimethylbenzil(**4**): ¹H NMR(CDCl₃) δ 2.42 (s, 6H), 7.26-7.48 (m, 5H), 7.91-7.94 (m, 3H); IR(KBr) 1688 cm⁻¹; ¹³C NMR(CDCl₃) δ 21.28, 127.42, 128.42, 129.34, 130.75, 134.57, 139.34, 172.23; mp. 101-103°C (lit.¹⁵ 102-104°C).

4,4'-Dinitrobenzil(**5**): ¹H NMR(DMSO-d₆) δ 8.18-8.31 (m, 8H); IR(KBr) 1691 cm⁻¹; ¹³C NMR(DMSO-d₆) δ 122.75, 130.22, 136.17, 149.68, 165.76; mp. 214°C (lit.¹⁶ 213°C).

4,4'-Dihydroxybenzil(**6**): ¹H NMR(DMSO-d₆) δ 6.92 (d, J=8Hz, 4H), 8.05 (d, J=8Hz, 4H), 9.61 (bs, 2H); IR(KBr) 1700 cm⁻¹; ¹³C NMR(DMSO-d₆) δ 115.70, 121.95, 127.79, 132.47, 164.88; mp. 245-246°C (lit.¹⁷ 245-247°C).

3,3'-Dicarboxybenzil(**7**): ¹H NMR(DMSO-d₆) δ 7.50-7.61 (m, 3H), 8.18-8.23 (m, 5H); IR(KBr) 1693 cm⁻¹; ¹³C NMR(DMSO-d₆) δ 127.61, 130.12, 130.58, 132.79, 166.70; mp. 295°C.

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XPS Studies of Oxygen Adsorption on Polycrystalline Nickel surface (II)

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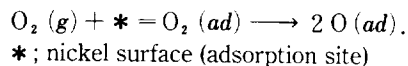
The isotherms of oxygen chemisorption on polycrystalline nickel surface are obtained at various temperatures between 298K and 523K from intensity measurement of O 1s xps peaks, and the activation energy of the chemisorption is estimated as a function of the coverage. The activation energy extrapolated to zero coverage is found to be -5.9kJ/mol. The negative activation energy can be taken as a strong implication of the propriety of a currently accepted chemisorption model, in which molecularly adsorbed precursor state is assumed to exist. The residence time of this precursor state is estimated by assuming a molecularly physisorbed state for the precursor state and assuming a pairwise interaction energy of Lennard-Jones 12-6 potential between an admolecule and each substrate nickel atom. The sticking coefficients are also calculated from the isotherms. The calculated results agree well with those obtained by others with different methods.

Introduction

In our previous report of xps studies of oxygen adsorption on polycrystalline nickel surface¹, it is reported that the O 1s xps peak at 530.2eV(binding energy) due to the dissociatively adsorbed oxygen atoms appears in the early stage of oxygen exposure at all the temperature range of experiment but the highest one at 523K. It is also reported that this dissociatively adsorbed oxygen species is responsible for the formation of p(2 × 2) and c(2 × 2) oxygen layer structures on Ni(100) surface. On further oxygen exposure, this species forms surface oxide layer, showing additional peaks at 531.3 eV and 529.7eV. The rate of this oxide layer formation decreases with increase in temperature. It is certain that an attempt to kinetic explanation for these observed results will augment the hitherto known knowledge of the oxygen chemisorption mechanism.

There have been a lot of studies on the mechanism of oxygen-nickel surface interaction systems, especially by means of AES and LEED^{2,3} and photoelectron spectroscopy^{4,7}. Most of the results are summarized in recent review articles^{8,9}. For a reasonable explanation for these experimental

findings, it is generally assumed that oxygen is chemisorbed dissociatively through a molecularly adsorbed precursor state as following;



Brundle *et al*⁷ observed that the sticking coefficient of oxygen molecule on the Ni(100) surface decreases linearly with the increasing oxygen coverage according to (1-4θ) at 300K, θ being the coverage. To explain the findings with the assumed model described above, they have further assumed that the molecularly adsorbed species has a so short residence time on the nickel surface that the rate of overall oxygen chemisorption is hardly influenced by temperature change at these elevated temperature range. On the other hand, they found a very high sticking coefficient at 77K, approaching almost unity up to higher coverage. They have assumed this temperature is low enough to hold the molecularly adsorbed species very long and thereby resulting in such a high sticking coefficient.

In spite of all these assumptions, no experimental evidence of the molecularly adsorbed species has been ever