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DMSO-based Reagents for the Oxidation of Alkenes and Alkynes to 1,2-Diketones

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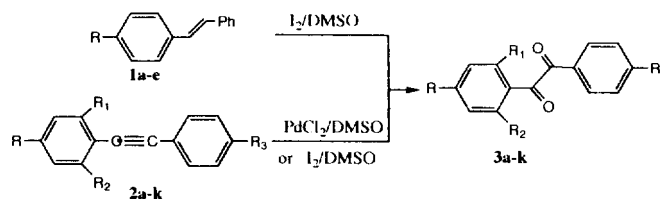
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There has been a deficit of convenient and selective reagents for the oxidation of carbon-carbon double and/or triple bonds to 1,2-dicarbonyl compounds.¹ We have recently reported that a triple bond of 1,2-diarylethyne can be successfully oxidized to 1,2-diketone with iodine or palladium(II) chloride in DMSO.²⁻⁴

In this paper, we would like to report not only the relative

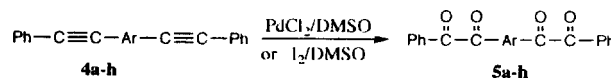
reactivity and selectivity of these DMSO-based reagents in the process of oxidation of 1,2-diarylethenes and/or 1,2-diarylethyne but also a new method using Pd/C with copper(II) halide in DMSO for the oxidation of 1,2-diarylethyne.



1-3	R	R ₁	R ₂	R ₃	1-3	R	R ₁	R ₂	R ₃
a	H	H	H	H	g	NO ₂	H	H	H
b	CH ₃	H	H	H	h	CH ₃	CH ₃	CH ₃	H
c	OH	H	H	H	i	CH ₃	H	H	CH ₃
d	OCH ₃	H	H	H	j	OCH ₃	H	H	OCH ₃
e	Cl	H	H	H	k	Cl	H	H	Cl
f	CHO	H	H	H					

Various 1,2-diaryl-1,2-ethanediones **3a-k** have been synthesized in good yields by heating corresponding diarylethenes **1a-e** or diarylethyne **2a-k** in DMSO with equimolar quantities of iodine (reagent A). (Table 1) With reagent A, the oxidation of tolans **2** turns out to proceed in two times, at least, faster than that of the corresponding stilbenes **1** and the oxidation rate has a tendency to decrease in the presence of electron-withdrawing substituent in the reactants **1** and **2**. It is also interesting to note that methoxy-substituted stilbene **1d** and tolans **2d, j** can be effectively oxidized with reagent A without iodination. However, heating hydroxy-stilbene **1c** or tolan **2c** with reagent A led to the formation of several unidentified iodine containing compounds.

In contrast with iodine, palladium(II) chloride in DMSO (reagent B) does not oxidize stilbenes **1** but shows high reactivity for the oxidation of tolans **2**. (Table 1) Besides its chemoselectivity, reagent B can oxidize **2c** to **3c** without producing any by-product. On the other hand, reagent B has been found to be more sensitive to the steric factor of substrates. For example, application of reagent B for the sterically hindered tolan **2h** produced benzil **3h** in 5% yield with a low conversion of **2h**. However, **2h** could be oxidized to **3h** in 33% yield with reagent A. It is noteworthy that smooth oxidation of triple bond in the labile tolan **2f** is effected by both reagents.



4, 5	Ar	4, 5	Ar
a		c	
b		f	
c		g	
d		h	

Table 1. Preparation of 1,2-Diketones **3^o** from Alkenes **1^s** and Alkynes **2^s**

Substrate	I ₂ /DMSO (Reagent A)				PdCl ₂ /DMSO (Reagent B)				mp °C	Lit. mp °C
	Temp. °C	Time hr	Yield ^b %	Product	Temp. °C	Time hr	Yield ^b %	Product		
1a	155	10	85	3a	140	10	0	3a	93-94	94-95 ²
2a	155	1	93	3a	140	4	98	3a	94-95	94-95 ²
1b	145	25	62	3b	—	—	—	—	oil	29-30 ⁴
2b	145	15	80	3b	—	—	—	—	27-29	29-30 ⁴
2c	135	6	0	3c	140	2	84	3c	128-129	129-130 ³
1d	145	9	80	3d	140	5	0	3d	60-61	63-64 ⁴
2d	145	4	90	3d	—	—	—	—	63-64	63-64 ⁴
1e	145	30	83	3e	—	—	—	—	68-71	73-74 ⁴
2e	145	14	86	3e	—	—	—	—	73-74	73-74 ⁴
2f	135	5	68	3f	110	22	68	3f	71-72	73-75 ⁷
2g	155	6	90	3g	145	4	60	3g	141-142	140-142 ²
2h	135	9	33	3h	140	33	5	3h	132-133	133-136 ⁸
2i	145	7	70	3i	—	—	—	—	99-102	100-101 ⁹
2j	145	2	92	3j	—	—	—	—	133-135	131-132 ⁹
2k	145	19	71	3k	140	6	86	3k	198-200	199-200 ⁹

^aAll the 1,2-diketones prepared are known compounds and identified by their melting points and spectral data. ^bYields refer to isolated, pure products.

Table 2. Preparation of Bis-1,2-diketones **5^o** from Diynes **4^o**

Substrate	Product	I ₂ /DMSO (Reagent A)			PdCl ₂ /DMSO (Reagent B)			mp °C	Lit. mp °C
		Temp. °C	Time hr	Yield ^b %	Temp. °C	Time hr	Yield ^b %		
4a	5a	155	22	90	145	10	80	124-125	124-125 ²
4b	5b	115	7	71	140	4	85	203-204	205-206 ¹¹
4c	5c	140	23	81	140	4	61	105-106	106-107 ¹¹
4d	5d	140	25	72	140	17	74	192-194	193-194 ¹¹
4e	5e	115	7	82	140	4	72	141-143	144-145 ¹⁰
4f	5f	140	28	76	140	2.5	80	130-131	128-130 ¹¹
4g	5g	155	18	68	155	1.5	73	239-241	239-241 ¹¹
4h	5g	115	7	71	115	2.5	67	239-241	239-241 ¹¹

^aAll the bis-1,2-diketones prepared are known compounds and identified by their melting points and spectral data. ^bYields refer to isolated, pure products.

Reagents A and B also have been effectively used for the oxidation of bis(phenylethynyl)arenes **4a-h** to bis(phenylglyoxalyl)arenes **5a-h** which are essential monomers for the synthesis of thermostable polymer-polyphenylquinoxalines.¹⁰

As shown in the Table 2, the oxidation of diynes **4** with both reagents gives high yields of tetraketones **5** and reagent B reveals higher reactivity than reagent A. The oxidation rate with reagent A becomes slow when an electron-withdrawing group is present in the reactants **4**. Both reagents oxidize the methylene group of fluorene moiety as well as the triple bonds in diyne **4h** to produce fluorenone **5g** as a major product. With reagent A, **5h**¹² was obtained from **4h** in 11% yield, at the best, along with the major product **5g** (71%). The fact that fluorene is not oxidized with reagents A and B under the same oxidation conditions for diyne **4h** is of interest.

A new oxidation method using heterogeneous catalysts-Pd/C with CuCl₂·2H₂O or CuBr₂ in DMSO has been developed for the oxidation of alkynes **2** and **4**. With this methodology, **2f** and **4a** have been successfully oxidized to **3f** (69%) and **5a** (76%) respectively. Addition of a catalytic amount of CuCl₂·2H₂O or CuBr₂ into the heterogeneous oxidation system is required since the oxidation without copper(II) halide proceeds too slow to be effected. Thus, copper(II) halide is believed to produce an active catalytic species of Pd²⁺. Due to the easiness of separation of catalysts from a reaction mixture, the heterogeneous catalytic oxidation of alkynes must be an useful alternative for industrial application.

General oxidation method using Pd/C with copper(II) halide: A mixture of 1,4-bis(phenylethynyl)benzene (**4a**) (280 mg, 1.01 mmol), Pd/C (100 mg, palladium content 0.8%), CuCl₂·2H₂O (34 mg, 0.20 mmol) in DMSO (10 mL) was heated

at 140 °C for 15 hours. The resulting mixture was filtered at room temperature for the removal of insoluble catalysts. The filtrate was diluted with water (30 mL) and extracted with diethyl ether (3×30 mL). The combined extracts were washed with water (20 mL), brine (20 mL) and dried over Na₂SO₄. The organic solvents were removed *in vacuo* and the crude product was purified by flash chromatography (50 % benzene-hexane) to afford 1,4-bis(phenylglyoxalyl)benzene (**5a**) (262 mg, 0.77 mmol) in 76% yield.

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12. mp 192-194 °C (isopropanol); ¹H NMR (100 MHz, CDCl₃) δ 7.30-8.10 (m, 16H), 4.92 (s, 2H); IR (CHCl₃) cm⁻¹ 1665 (C=O); C₂₅H₁₈O₄ calc. C 80.92 H 4.21 found C 81.20 H 3.94.