Iodine in Dimethyl Sulfoxide as a New General Reagent for the Preparative Oxidation of 1,2-Diarylethenes and 1,2-Diarylethynes to Aromatic 1,2-Diketones

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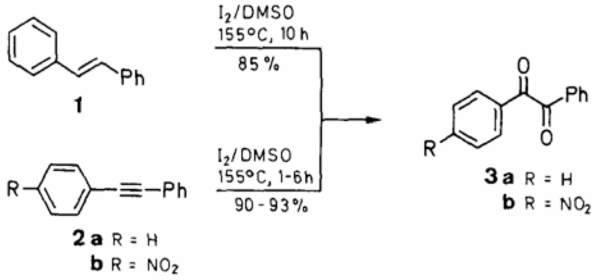
1,2-Diarylethenes and 1,2-diarylethynes are readily converted to the corresponding 1,2-diketones in high yield using the reagent iodine in dimethyl sulfoxide. Alkynes in these reactions are more reactive than alkenes.

Recently we discovered that hydrobromic acid in dimethyl sulfoxide is a convenient and gentle reagent for oxidation of 1,2-diarylethenes and of a number of vicinal substituted 1,2-diphenylethanes to 1,2-diaryl-1,2-ethanediones.[1-3] Diphenylethyne also undergoes partial oxidation to 1,2-diphenyl-1,2-ethanedione under the same conditions but is more than ten times slower compared to 1,2-diphenylethene. Therefore hydrobromic acid in dimethyl sulfoxide is not a suitable reagent for the preparative oxidation of triple bonds.

In this work we have found iodine in dimethyl sulfoxide to be a general reagent for the oxidation of multiple bonds in 1,2-diphenylethene (stilbene, **1**) and alkynes **2** to 1,2-diketones **3**.



The suggested oxidizing agent (iodine/dimethyl sulfoxide) does not break the C,C-bond, as arylcarboxylic acids or aldehydes are not found in the reaction products by TLC. The main advantage of this new method is the direct oxidation of multiple bonds giving 1,2-diketones without byproducts. The existing methods using reagents such as potassium permanganate, thallium nitrate, selenium dioxide, ruthenium tetroxide, ozone and others,[4] bis(trifluoroacetoxy)phenyliodine[5] to a greater or lesser extent completely break multiple bonds. It should be noted that bis(trifluoroacetoxy)phenyliodine, a selective reagent for the oxidation of triple bonds to 1,2-diketones, is not able to oxidize diarylethynes containing strong electron-withdrawing substituents.[6] However, iodine/dimethyl sulfoxide oxidizes successfully 4-nitrodiphenylethyne **2b** (Table).

Table. Preparation of 1,2-Diketones **3a**, **b**, **5**, **7**, **8** from Alkenes **1**, **4** and Alkynes **2a**, **b**, **6**[a]

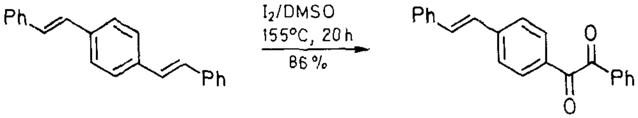
Substrate	Product	Time (h)	DMSO/Substrate (mL/mmol)	Yield[b] (%)	mp (°C) (solvent)	Molecular Formula or Lit. mp (°C)
1	**3a**	10	8	85	93–94 (EtOH)	94–95[1]
2a	**3a**	1	5	93	94–95 (EtOH)	94–95[1]
2b	**3b**	6	5	90	140–142 (EtOH)	141–142[2]
4	**5**	20	15	86	110–111 (EtOH)	$C_{22}H_{16}O_2$ (312.4)
6	**7**	22	10	90	124–125 (EtOH)	124–125[5]
6	**8**	17	10	45[c]	106–108 (hexane)	106–107[5]

[a] All the 1,2-diketones prepared are known compounds and identified by their physical properties and spectral data (mp, IR, ^{1}H-NMR).

[b] Yield of pure, isolated product.

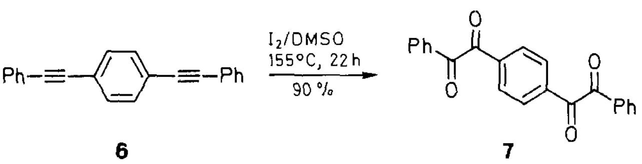
[c] Parent compound **6** was isolated together with compound **8** and separated by liquid chromatography (silica gel, benzene).

The fact that the oxidation of diarylethynes **2** occurs much faster than that of stilbene (**1**) under the same conditions (1 equivalent of iodine per 1 equivalent of substrate) is of interest. Furthermore, for the oxidation of **1** a somewhat greater quantitiy of dimethyl sulfoxide (8 mL per 1 mmol of substrate) is required than for the oxidation of the diarylethynes **2** (5 mL per 1 mmol). Electron-withdrawing substituents in the aryl groups of compounds **1** and **2** slow down the oxidation but in case of 1,2-diarylethenes this inhibition is much more noticeable. Thus, 1-(4-nitrophenyl)-2-phenylethyne gives only traces of the diketones **3b** together with the parent compound by treatment with iodine/dimethyl sulfoxide at 160 °C for 18 h. This inhibition of oxidation reaction of alkenes by electron-withdrawing substituents allowed selective oxidation of only one double bond in (*E,E*)-1,4-bis(2-phenylethenyl)benzene (**4**) to give the 1,2-diketone **5** in high yield.



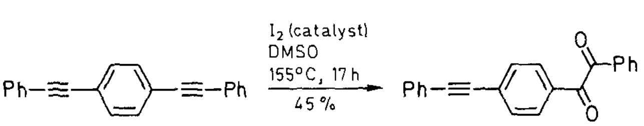
4 **5**

Under the same conditions 1,4-bis(phenylethynyl)-benzene (**6**) is readily oxidized to 1,4-bis(phenylglyoxaloyl)benzene (**7**).



6 **7**

Decreasing the quantity of iodine almost to a catalytic amount (0.02 equivalent of iodine per 1 equivalent of substrate) allowed the selective oxidation of one triple bond in compound **6**.



6 **8**

Thus, iodine/dimethyl sulfoxide is a novel reagent in its selectivity, mildness of the conditions and convenience of use for direct oxidation of double and triple bonds to aromatic 1,2-diketones. Iodine/dimethyl sulfoxide is more reactive for the oxidation of triple bonds as well as to reagents like for example such as hydrobromic acid/dimethyl sulfoxide, is more reactive in the oxidation of double bonds.[1-3]

I_2 was used of quality "purity from analysis", DMSO, Stilbene (**1**) and diphenylethyne (**2a**) were used of quality "chemical purity" without further purification. (4-Nitrophenylphenylethyne (**2b**) and 1,4-bis(phenylethynyl)benzene (**6**) were prepared according to *Lit.*[7] from 4-nitroiodobenzene and 1,4-diiodobenzene, respectively and phenylethyne cuprate. (*E,E*)-1,4-bis(2-phenylethenyl)benzene (**4**) was prepared by Wittig reaction as described.[8] Analytical TLC plates (Silufol UV-254) and silica gel LS_{254} 5/40 μ were purchased from Chemapol. IR spectra were obtained using a Carl Zeiss UR 20 spectrophotometer. ^{1}H-NMR spectra were obtained using a Tesla BS 567A 100 MHz spectrometer.

1,2-Diphenyl-1,2-ethanedione (3a) from Stilbene (1):

A mixture of stilbene (**1**; 0.18 g, 1 mmol), I_2 (0.25 g, 1 mmol) and DMSO (8 mL) is heated at 155 °C for 10 h. The solution poured into 1 % aq $Na_2S_2O_3$ (20 mL), yellow crystals precipitated are filtered, washed with H_2O and dried; yield: 0.18 g (85 %); mp 93–94 °C (Lit.[1] mp 94–95 °C).

1,2-Diketones from Diarylethynes 2, General Procedure:

A mixture of diarylethyne (2.1 mmol), I_2 (0.25 g, 1 mmol) and DMSO (5 mL) is heated at 155 °C for time given in Table. The products are isolated by the procedure given for compound **1**.

1-(Phenylglyoxaloyl)-4-(phenylethenyl)benzene (5):

A mixture of (*E,E*)-1,4-bis(phenylethenyl)benzene (**4**; 0.28 g, 1 mmol), I_2 (0.5 g, 2 mmol) and DMSO (15 mL) is heated at 155 °C for 20 h. The product is isolated by the procedure described above; yield: 0.27 g (86 %); mp 110–111 °C (EtOH).

$C_{22}H_{16}O_2$	calc.	C 84.59	H 5.16
(312.4)	found	84.76	5.40

IR (Nujol): ν = 1610 (C=C), 1680 (C=O), 980 cm^{-1} (=C–H).

^{1}H-NMR ($CDCl_3$/TMS): δ = 7.18 (d, 1 H, J = 15.9 Hz, PhC$\underline{H}$=CH), 7.52 (d, 1 H, J = 15.9 Hz, PHCH=C$\underline{H}$), 7.15–7.86 (m, 10 H_{arom}), 7.91 ppm (d, J = 7.1 Hz, 4 H_{arom}).

1-(Phenylglycoxaloyl)-4-(phenylethynyl)benzene (8):

A mixture of 1,4-bis(phenylethynyl)benzene (**6**; 0.28 g, 1 mmol), I_2 (5 mg, 0.02 mmol) and DMSO (10 mL) is heated at 155 °C for 17 h. The product is isolated by the procedure described above and is purified by liquid chromatography (silica gel, benzene, it is also possible to use toluene, as eluent); yield: 0.14 g (45 %); mp 106–108 °C (hexane) (Lit.[5] mp 106–107 °C).

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