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Formation of *cis*-1,2-Dibenzoylethylene from 2,5-Diphenylfuran by Fenton's Reagent and by Peroxydisulfate. Effect of Oxygen

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The formation of *cis*-dibenzoylethylene from 2,5-diphenylfuran has been used as a probe for singlet oxygen. However, work by Takayama et al.[1] has shown that the reaction of Udenfriend's reagent (Fe^{2+}–EDTA–ascorbic acid–O_2)[2] also gives rise to *cis*-dibenzoylethylene, therefore making this probe nonspecific for singlet oxygen. Takayama et al.[1] concluded that for the formation of *cis*-dibenzoylethylene both OH radicals and O_2 are necessary. This conclusion was based on the claim by King et al.[3] that under a nitrogen atmosphere 2,5-diphenylfuran did not react with Fenton's reagent. This claim is indeed amazing considering the high reactivity of OH radicals. The rate constants of OH radicals with aromatic compounds are in the order of 10^9–10^{10} M^{-1} s^{-1}.[4] However, a careful examination of the experimental data of King et al.[3] shows that their conclusion is incorrect. Their reaction mixture contained, in addition to Fe^{2+}, EDTA, and H_2O_2, 30 mM ascorbic acid and 1 mM diphenylfuran. Under these conditions all the OH radicals react with ascorbic acid and no reaction product from diphenylfuran is expected. Our results on the reaction of diphenylfuran with Fenton's reagent are shown in Table I. In both sets of experiments (in the absence or presence of oxygen) we obtained good yields of *cis*-dibenzoylethylene. The mechanism is shown in Scheme I.

Table I. Oxidation of 2,5-Diphenylfuran by Fenton's Reagent. Effect of O_2 and pH

reactn condns[a]				
H^+	Ar/O_2	*cis*-DBE[b] (mol × 10^6)	-DPF[c]	% yield
H^+	Ar	53	102	52
H^+	O_2	135	225	60
	Ar	70	115	61
	O_2	103	188	55

[a] All reactions contained 0.25 × 10^{-3} mol of DPF in 25 mL of CH_3CN/25 mL of H_2O. The experiments in the presence of H^+ contained 250 µL of concd $HClO_4$. For details see Experimental Section. [b] *cis*-DBE: *cis*-1,2-dibenzoylethylene. [c] DPF: 2,5-diphenylfuran.

Scheme I

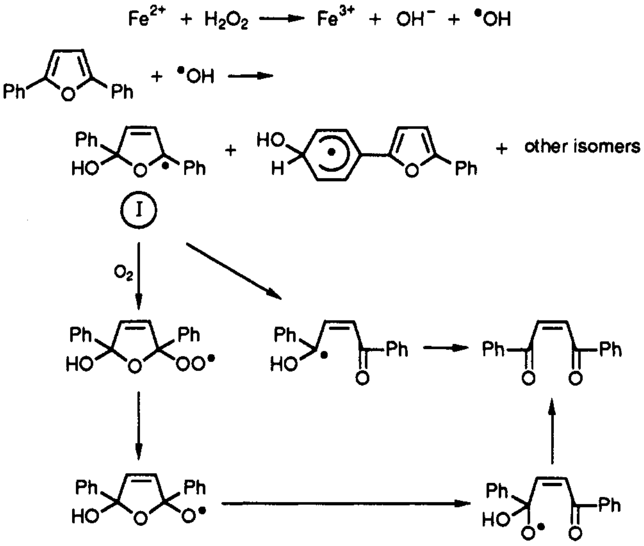
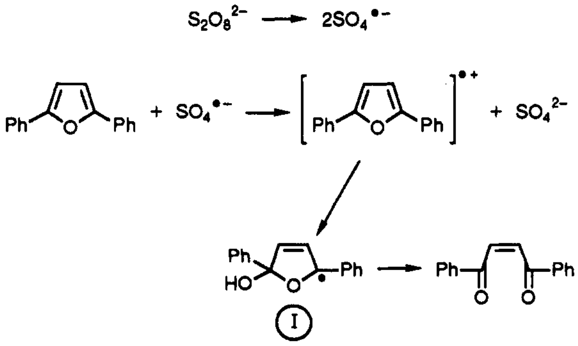


Table II. Oxidation of 2,5-Diphenylfuran by Thermal Decomposition of Peroxydisulfate

reactn condns[a]		temp		*cis*-DBE[b]		
$S_2O_8^{2-}$ (mol)	Ar/O_2	(°C)	time	(mol × 10^6)	-DPF[c]	% yield
0.5 × 10^{-3}	Ar	70	30 min	59	60	97
	Ar		1 h	104	119	87
	O_2		30 min	73	75	97
	O_2		1 h	145	150	97
2.5 × 10^{-3}	O_2	25	48 h	57	100	57
	O_2		72 h	77	125	62
	O_2		8 days	186	250	74

[a–c] See footnotes, Table I.

Scheme II



Hydroxyl radical adducts of aromatic compounds can be obtained by two distinct routes: (1) addition of OH radicals or (2) oxidation of the aromatic to a radical cation, followed by nucleophilic addition of H_2O. In the hydroxylation of some simple monosubstituted benzenes it has been shown that these two methods lead to different isomer distributions.[5] In a recent paper[6] we have shown that the oxidative cleavage of *trans*-stilbene to benzaldehyde proceeds both via OH radicals and via the stilbene radical cation. We have shown that the radical cation route leads to considerably higher yields of benzaldehyde. This is due to the fact that addition of H_2O to the stilbene radical cation takes place at the double bond and not at the ring positions, whereas addition of OH radicals takes place at both the double bond and at the ring positions. We therefore expect a higher yield of intermediate I (Scheme I) in the reaction of diphenylfuran with $S_2O_8^{2-}$ compared to the reaction with Fenton's reagent. Our results (Table II) clearly support this conclusion. The reactions are shown in Scheme II. The reaction with peroxydisulfate can be carried to the complete comsumption of diphenylfuran. It is a convenient method for the synthesis of *cis*-dibenzoylethylene.

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Conclusion. Our results show that 2,5-diphenylfuran reacts with Fenton's reagent (Fe^{2+}–H_2O_2) both in the presence or absence of oxygen to give good yields of *cis*-1,2-dibenzoylethylene. The reaction of 2,5-diphenylfuran radical cation with water takes place exclusively at the 2-position of the furan ring to give *cis*-1,2-dibenzoylethylene in quantitative yield. In none of these described reactions is any singlet oxygen involved.

Experimental Section

Materials. The reagents were obtained from the following sources: $K_2S_2O_8$, $Fe(NH_4)_2(SO_4)_26H_2O$, H_2O_2(30%) from Fisher Scientific, *trans*-1,2-dibenzoylethylene from Aldrich Chemical Co., and 2,5-diphenylfuran from Kodak. The *cis*-1,2-dibenzoylethylene was prepared from the trans isomer by the method of Conant and Lutz.[7]

Methods. (1) Fenton reaction. A solution of 25 mL of CH_3CN/25 mL of H_2O containing 0.25×10^{-3} mol of 2,5-diphenylfuran (0.5×10^{-2} M) was deoxygenated by bubbling argon through the solution for 15 min. In some othe experiments the solution was saturated with oxygen. After the Argon bubbling Fe^{2+} (0.5×10^{-3} mol) was added and finally H_2O_2 (100 μL 30%, 0.88×10^{-3} mol) was injected through a rubber septum. Analysis was carried out after 30 min reaction time. (2) Peroxydisulfate oxidation. A solution of 25 mL of CH_3CN/25 mL of H_2O containing 0.25×10^{-3} mol of 2,5-diphenylfuran and $K_2S_2O_8$ was saturated with either argon or oxygen for 15 min. Then the bottle was stoppered and heated in a hot water bath.

Analysis. The analyses were carried out with a Waters HPLC equipped with dual pump and solvent programming. The column was a 1-ft C_{18}-μ-Bondapak reversed-phase column. The solvents were CH_3OH/H_2O programmed from 30% CH_3OH to 85% CH_3OH in 20 min at 1 mL/min. Standard solutions were analyzed for calibration.

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