

Tetraphenylcyclopentadienone의 고체상 광산화반응

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A Photooxidation in Solid State on Tetraphenylcyclopentadienone

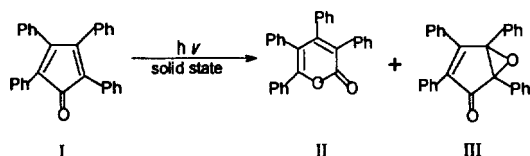
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Organic acid state chemistry has grown rapidly and vigorously during the last decade.¹ The oxidation of tetraphenylcyclopentadienone results in various products depending on the condition used.² The oxidation is accompanied by the loss of the characteristic color. Under slightly strong oxidation conditions, namely nitric acid in acetic acid at 100 °C, tetraphenyl-2-pyrone was obtained.³ Refluxing tetraphenylcyclopentadienone with acetic acid, acetic anhydride, and hydrogen peroxide produced mainly tetraphenyl-2-pyrone.⁴ Tetraphenylcyclopentadienone was photooxidized in solution phase, which gave *cis*-dibenzoylstilbene, *trans*-dibenzoylstilbene and tetraphenyl-2-pyrone.⁴

In this letter we examined on the simple and convenient synthesis of tetraphenyl-2-pyrone **II** from tetraphenylcyclopentadienone **I** as organic solid state in high yield.



Irradiation of **I** in solid state as a thin film with high pressure mercury lamp under atmosphere at room temperature for 2 hrs gave **II** and **III** in 96% and 4% yields, respectively. The structure of **II** and **III** was elucidated on the basis of spectral properties and elemental analysis,^{5,6} and that of

II was confirmed by direct comparison of its IR and NMR spectra with an authentic sample.³ The IR spectrum of **II** showed an absorption at strong 1690 cm⁻¹ assignable to the carbonyl group of pyrone, while that of **III** showed absorption at 1705 cm⁻¹ due to a carbonyl group of the epoxyketone. The ¹³C NMR spectrum of **II** showed a signal characteristic of carbonyl carbon 168.7 ppm, while that of **III** showed it at higher field, 198.1 ppm.

The influence of conditions to oxidation of **I** on product was also studied. Neither compound **II** nor compound **III** could be obtained under irradiation of an solid phase of **I** in the absence of oxygen under condition described above. Compound **II** and **III** thus obtained were indefinitely stable in the solid state at room temperature. Compound **II** was recovered unchanged even when heated to reflux in dichloromethane for a long time. On the other hand, the thermal epoxide ring opening of **III** to **II** was observed.

Thus, irradiation in the solid state as thin film provide synthetically useful selective photooxidation method for tetraphenylcyclopentadienone.

General procedure. Compound **I** was dissolved in dichloromethane, that was coated on the normal glass plate (20×20 cm) as thin film. The solid state thin film of **I** was irradiated with 450W high pressure mercury lamp for 2 hrs at room temperature under atmosphere. The photooxidation was determined by the loss of the characteristic purple co-

lor. The compound on the glass was extracted with dichloromethane, and the solvent was evaporated. The products were purified by preparative thin layer chromatography on silicagel or column chromatography on silica gel. The compounds were characterized by physical and spectral data.^{5,6}

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5. Data for II: White needle crystal, mp 166~167 °C; R_f (silica gel, dichloromethane/hexane, 4 : 1)=0.6; UV(hexane) λ_{max} =236 nm(ϵ 16,300) and 259 nm(ϵ 14,200); IR(KBr) 1690(s), 1418(m), 1220(s), 730(m) cm^{-1} ; elemental analysis(Calcd. C: 86.97, H: 4.99, Found. C: 86.92, H: 4.95); HRMS Found 400.4729, Calcd. for $C_{29}H_{20}O_2$ 400.4757; 1H NMR($CDCl_3/TMS$) δ 7.10~7.85(5 H, m, PhH); ^{13}C NMR($CDCl_3/TMS$) δ 124.7, 128.4, 131.2, 136.3, 136.7, 137.8, 140.1, 141.2, 168.7.
6. Data for III: Yellow crystal, mp 152~153 °C; R_f (silica gel, dichloromethane/hexane, 4 : 1)=0.35; UV(hexane) λ_{max} =235 nm(ϵ 15,200), 240 nm(ϵ 8,100), and 350 nm(ϵ 4,800); IR(KBr) 1705(s), 1470~1530 (m) and 600(s) cm^{-1} ; elemental analysis(Calcd. C: 86.97, H: 4.99, Found. C: 86.92, H: 5.00); HRMS Found 400.4733, Calcd. for $C_{29}H_{20}O_2$ 400.4758; 1H NMR($CDCl_3/TMS$) δ 6.82~7.32(5 H, m, PhH); ^{13}C NMR($CDCl_3/TMS$) δ 128.2, 129.1, 130.7, 133.7, 134.2, 134.2, 155.0, 156.6, 198.1.