

단 신

실리카겔에 의한 Tetraphenylcyclopentadienone의 산화

李愚鵬* · 申賢珠 · 吳東元 · 黃惠海 · 鄭宰準†

경북대학교 화학과

†한국 기초 과학 지원연구소 핵자기공명팀

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New Convenient Oxidation of Tetraphenylcyclopentadienone by Silica Gel

Woo-Bung Lee*, Hyun-Ju Shin, Dong-won Oh, Dug-hea Hwang, and Chaejoon Cheong†

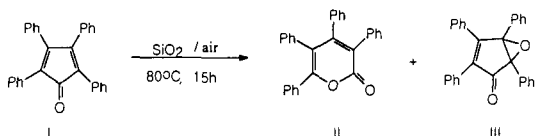
Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea

†Magnetic Resonance Group, Korea Basic Science Institute, Yusong P.O. Box 41, Taejeon 305-333, Korea

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The properties of organic molecules are considerably changed when the molecules are adsorbed on solid surfaces.¹ The oxidation of tetraphenylcyclopentadienone results in various products depending on the reaction conditions.² This oxidation is accompanied by the change of the characteristic color. Under slightly strong oxidation conditions, namely nitric acid in acetic acid at 100 °C, tetraphenyl-2-pyrone was obtained.³ When a solution of tetraphenylcyclopentadienone with acetic acid, acetic anhydride, and hydrogen peroxide was refluxed, tetraphenyl-2-pyrone was mainly obtained.^{4a} Tetraphenylcyclopentadienone was photooxidized in a solution phase to give *cis*-dibenzoylstilbene, *trans*-dibenzoylstilbene, and tetraphenyl-2-pyrone.^{4b,c}

In this letter, we report a simple and convenient synthesis of tetraphenyl-2-pyrone **II** from tetraphenylcyclopentadienone **I** by silica gel catalysis in solid phase.



When tetraphenylcyclopentadienone **I** was heated at 80 °C for 15h with the usual chromatographic grade silica gel (ratio of SiO₂ : **I** from 10 to 20:1), the oxidation occurred effectively to produce tetraphenyl-2-pyrone **II** in 94% yield. These conditions are considerably milder

than those oxidations under liquid phase conditions.³ Using the silica gel activated by drying at 200°C for 10 h to physically remove all adsorbed water, the reaction proceeded rapidly within 2 h at 60°C. The rate of conversion at 60°C depends on the ratio of SiO₂ : **I**, w/w. Thus, a complete conversion is achieved within 2 h for r=10:1, while the conversion rate is dropped to 10-40% for r=20:1 under the same condition (see general procedure⁵).

Chromatographic silica gels of different brands (FRG, Woelm, 5/20 μ, 100/160 μ, Mallinckrodt, <150 μ) are comparable in activity. Magnesium silicate (FRG, florisil, Merck 75/150 μ) was somewhat less active (even after activation) and required higher temperature (by 120-150°C) to obtain results comparable with those on dry SiO₂. The use of chromatographic alumina (FRG, Merck) led to poorer results mainly due to the formation of side product **III**. The addition of solvents (especially polar) lowered the conversion rate.

The structures of **II** and **III** are elucidated on the basis of their spectral and elemental analysis,^{5,7} and that of **II** was conformed by direct comparison of its IR and NMR spectra with an authentic sample.³ The IR spectrum of **II** showed a strong absorption band at 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 at δ

168.5 ppm, while that of **III** showed it at δ 198.1 ppm.

It seems very difficult to provide a plausible explanation for the promotion effect by the adsorption as shown in this reaction due to the complicated effects of adsorbate-adsorbent interactions. There are many data available from the studies in the field of heterogeneous catalysis which attest to the importance of this effect for various reactions.⁸

Thus, the use of adsorbents as active supports and catalysts provides a synthetically useful oxidation method for tetraphenylcyclopentadienone. The detailed study of cyclopentadienone derivatives is currently under investigation and the results of these studies will be reported in due course.

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5. A general procedure is as follows: To a compound I was added SiO₂ (Woelm 100/160 μ , dried at 200 °C for 10h; ratio r=10:1). The mixture was shaken vigorously and allowed to stand at 80°C for 15h in a stoppered flask. After cooling, extraction with ether, solvent removal and purification of the residue by preparative thin-layer chromatography on silica gel(dichloromethane : hexane=4:1) gave **II** in 94% yield together with minor product **III** (5~6%).
6. Data for **II**: White needle crystal, m.p.166~167 °C; R_f 0.6(dichloromethane: hexane=4:1); UV(hexane) λ_{\max} 236nm(ϵ 16,300) and 259nm(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 C₂₉H₂₀O₂ 400.4758; ¹H-NMR(CDCl₃) δ 7.10-7.85(5H, m, PhH); ¹³C-NMR(CDCl₃) δ 124.7, 128.4, 131.2, 136.3, 136.7, 137.8, 140.1, 141.2, 168.5.
7. Data for **III**: Yellow crystal, m.p.152~153; R_f =0.35 (dichloromethane : hexane=4:1); UV(hexane) λ_{\max} 235 nm(ϵ 15,200), 240nm(ϵ 8,100), and 350nm(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 C₂₉H₂₀O₂ 400.4758; ¹H-NMR(CDCl₃) δ 6.82-7.32(5H, m, PhH); ¹³C-NMR(CDCl₃) δ 128.2, 129.1, 130.7, 133.7, 134.2, 155.0, 156.6, 198.1.
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