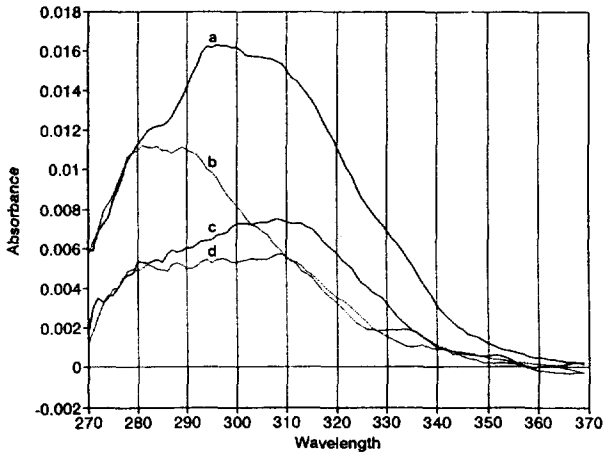
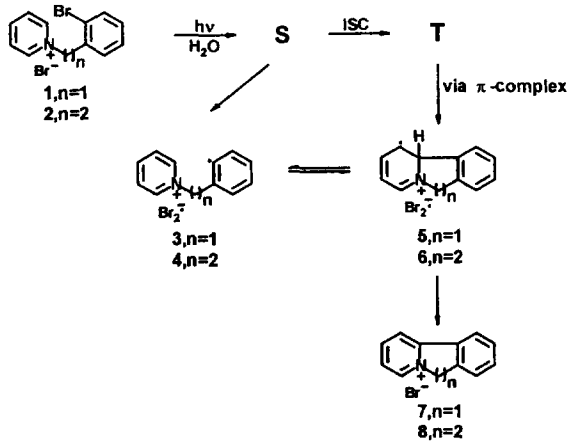


Figure 2. Transient absorption spectra acquired at 300 μs following the 266 nm excitation of 1×10^{-4} M aqueous solution of *N*-(2-bromophenyl)alkylpyridinium salts. (a) Ar bubbled **2**, (b) O_2 bubbled **2**, (c) Ar bubbled **1**, (d) O_2 bubbled **1**.



Scheme.

μs delay after laser-irradiation of aryl bromides **1** or **2** is observed (see Figure 2). (2) The absorption is diminished extensively in the O_2-saturated solution, probably because the transient is originated from triplet state of **1**, and therefore is quenched by oxygen. (3) The transient is not affected by the presence of N_2O or *N-tert*-butyl-α-phenyl nitrone. (4) The decay constant ($k=4\times10^2$ s^{-1}, see Table) is much smaller value than that of triplet-triplet absorption. (5) The transient around 310 nm is not observed from the photolysis of *N*-benzylpyridinium bromide, even though a small peak around 330 nm is observed. The physical properties of the transients are summarized in Table.

In conclusion, the detection of phenyl (**3** or **4**), conjugated pyridinium (**5** or **6**), and bromine anion radical as the transients in a photolysis of the aqueous pyridinium salt (**1** or **2**) confirms radical reaction in the photocyclization (see scheme). The dihydropyridinium radical (**5** or **6**) is formed from the phenyl radical (**3** or **4**) and triplet state *via* a π-complex[3] of the pyridinium salt, and in turn the phenyl radical is populated from singlet state of the pyridinium salts (**1** or **2**).

Acknowledgement. We acknowledge financial supports from The Korea Science and Engineering Foundation, and Korea Research Foundation through ICNSRF.

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Bulky Mono-substituted Catechol and *ortho*-Benzoquinone: Crystal Structure of 4-(2-phenyl-isopropyl)-*ortho*-benzoquinone

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o-Quinones are typical noninoncent bidentate O,O'-coordinators which are capable of undergoing intramolecular electron-transfer processes between transition metal and the ligand.[1,2] Many of the interesting and important features of *o*-quinone ligands are related to the similarity in energy between the quinone π*-orbitals and the metal *d*-levels.[3,4] Energetic proximity of several possible redox states leads to very diverse and intriging structural chemistry, redox reactivity, spectroscopy, and magnetochemistry and to their possible applications as molecular magnets and optical memories based on optical bistability.[1,2,5-12] Thus, the synthesis of new catechol and *o*-benzoquinone has considerable attention since there have been delicate and subtle differences in physicochemical properties for the metal complexes of the ligands. The alkylation of catechol with isobutylene yielded 3,6-di(*tert*-butyl)catechol with small quantity of 3,5-analog.[13]. On using isopentene and styrene instead of isobutylene, in addition to the ortho derivatives a small amount of 4-alkyl-substituted product was formed.[13] In the present work, the reaction of catechol with bulky α-methylstyrene is carried out and characterized. Herein we wish to report the preparation and properties of the title compound together with X-ray crystal

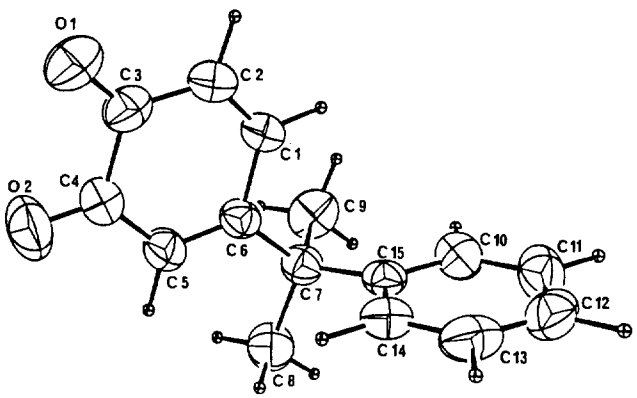
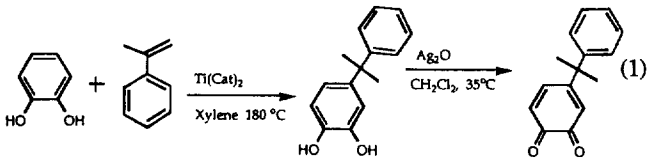


Figure 1. ORTEP drawing of 4-(2-phenyl-isopropyl)-o-benzoquinone with thermal ellipsoids shown at the 50% probability. Selected mean bond distances (Å) and angles (deg.): C3-O1, 1.220 (4); C4-O2, 1.211 (4): Cl-C2, 1.338 (4); C2-C3, 1.442 (5); C3-C4, 1.548 (5); C4-C5, 1.449 (4); C5-C6, 1.349 (4); C10-C11, 1.398 (5); C11-C12, 1.367 (6); C12-C13, 1.379 (5); C13-C14, 1.389 (5); C14-C15, 1.387 (4); C10-C15, 1.385 (4); C2-C3-O1, 124.4 (3); C4-C3-O1, 119.1 (2); C2-C3-C4, 116.5 (3); C6-C7-C8, 111.7 (3); C6-C7-C9, 107.2 (2); C6-C7-C15, 107.9 (2); C9-C7-C15, 112.7 (3); C8-C7-C15, 108.9 (3); C8-C7-C9, 108.3 (2).

structure. Study for the transition metal complexes of the ligand is interestingly underway.

Reaction[14] of catechol with α-methylstyrene in the presence of catalyst in stainless steel bomb at 180℃ affords only 4-(2-phenyl-isopropyl)catechol in 60% yield (eq. 1). The pro-



duct is established by elemental analysis, ^{1}H-NMR, and ^{13}C-NMR. The 4-(2-phenyl-isopropyl)catechol is stable colorless crystals which are soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, acetone, toluene, but insolube in hexane and petroleum ether. When the reaction was attempted in the absence of xylene as solvent, the yield is very low. The reaction nearly did not proceed in the absence of the catalyst, titanium catecholate. This reaction is moderately low yield (60%) and needs a long time (12 h) even though the reaction condition is more vigorous than that (96%) for 3,6-di(*tert*-butyl)catechol. This result is consistent that the rate of the reaction depends upon the stability of the carbonium ion being formed. As expected, the carbonium ion of *tert*-butyl group is more stable than that of 2-phenyl-isopropyl group. The most striking feature is that the reaction produces only monosubstituted product instead of the di-substituted mixture of 3,6- and 3,5-product formed from the reaction of catechol with isobutylene.[13] The present reaction is different from the reaction of catechol with styrene or isopentene, which afforded main product of *ortho*-derivative (for-OH group) in addition to a small amount of 4-alkyl-substituted analogue.[13] The formation of the mono-substituted catechol in the reaction is intrinsic and is not the result of a particular synthetic strategy. Why the product in the reaction is only mono-substituted product, rather than di-substituted, is not clear. There is a temptation to invoke the steric influence of the bulky 2-phenyl-isopropyl group.

The new 4-(2-phenyl-isopropyl)catechol is smoothly oxidized by general procedure using silver oxide in dichloromethane to give 4-(2-phenyl-isopropyl)-*o*-benzoquinone.[15] The *o*-benzoquinone is stable brown crystals with sharp melting point and soluble in most organic solvents. The crystal structure[16] along with selected bond lengths and bond angles is depicted in Figure 1. Relevant bond lengths and bond angles are appreciable. An interesting feature is the bond lengths of the benzoquinone ring: the bond lengths of C1-C2 (1.338 (4) Å) and C5-C6 (1.349 (4) Å) are much shorter than those of C2-C3 (1.442 (5) Å), C3-C4 (1.548 (5) Å), and C4-C5 (1.449 (4) Å). The specific bond lengths for the benzoquinone ring indicate that the ring is not completely aromatic system. In contrast, the six bond lengths of phenyl ring in the compound are validly delocalized.

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14. Preparation of 3-(2-phenylisopropyl)catechol. An autoclave was charged with 40 g (360 mmol) of catechol, 46 g (360 mmol) of α-methyl styrene, 1.2 g of titanium catecholate, 40 mL of xylene. The reaction was performed at 180℃ for 12 h and the solvent was evaporated. Addition of excess hexane precipitated black solid in 60% yield. Several recrystallizations of the crude product from a solvent pair of $CHCl_3$/hexane (1/1) gave white crystalline solids. mp. 98℃. Anal. found (Calcd. for $C_{15}H_{16}O_2$): C, 79.2 (78.9); H, 7.2 (7.1). IR (KBr, cm^{-1}): ν (O-H), 3490, 3354. ^{1}H-NMR (δ, ppm): 1.55 (s), 6.52 (d), 6.63 (d), 7.15 (m), 7.21 (m), 8.65 (d). ^{13}C-NMR (δ, ppm): 30.6, 41.6, 114.6,

116.8, 125.2, 126. 3, 127.8, 141.3, 143.0, 144.5, 150.9.
15. Preparation of 4-(2-phenyl-isopropyl)-*o*-benzoquinone. 10 g (29 mmol) of 3,6-bis(2-phenylpropyl)catechol and silver oxide 14.72 g (64 mmol) in 50 mL of dichloromethane were stirred for 6 h at 35℃. Evaporation of the solvent gave a brown solid in 90% yield. The crude solid was recrystallized from hexane to obtain brown crystals. mp. 65℃. Anal. found (Calcd. for $C_{15}H_{14}O_2$): C, 79.4 (79.6): H, 6.3 (6.2). IR (KBr, cm^{-1}): ν (C-O), 1660. ^{1}H-NMR (δ, ppm): 1.51 (s), 6.24 (d), 6.40 (d), 6.70 (q), 7.27 (m), 7.35 (d). ^{13}C-NMR (δ, ppm): 26.9, 43.2, 124.0, 126.6, 128.7, 141.1, 144.8, 159.1, 180.1. All spectroscopic data are available by ordering information.
16. Crystallographic Analysis. All the crystallographic data were obtained on an Enraf-Nonius CAD 4 automatic diffractometer with graphite-monochromated molybdenum radiation at ambient temperature. Preliminary diffractometric investigation indicated triclinic $P\bar{1}$ ($C1_i^1$, No. 2). Accurate cell dimensions were obtained from the setting angles of 25 well-centered reflections by using a least-square procedure. The data were corrected for Lorentz-Polarization effect, decay, and absorption with ψ-scan data. The structure was solved by a direct method, followed by successive difference Fourier synthesis. The non-hydrogen atoms were refined anisotropically by using SHELX-76. Hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. a=9.686 (2), b=10.894 (5), c=12.947 (3) Å, α=74.32 (2), β=82.68 (2), γ=68.54 (3), V=1223.5 (7) Å^3, Scan method=ω/2θ, No. unique data>3σ (I)=2087, R (Rw)=0.047 (0.055). All crystallograpic data (coordinates, anisotropic thermal parameters, bond distances and angles, structure factors) are available from OSJ of authors.

Diastereoselective Reduction of Chiral 2-(1,3-Oxazinyl) 2-Furylketone: Asymmetric Synthesis of (R)-(+)-2-(1,2-Dihydroxyethyl)furan

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Optically active 2-furylcarbinols serve as useful synthetic intermediates,[1] as they can be converted into 2-alkoxy carboxylic acids[2] or 2*H*-pyran-3-(6*H*)-ones[3] by various oxidative procedures. Therefore, much effort has been directed to the preparation of optically active 2-furylcarbinols.[4]

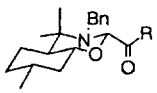
Recently, the bicyclic 2-(1,3-oxazinyl) ketones **1** derived from (R)-(+)-pulegone have been found to undergo highly stereoselective addition reaction with Grignard, organolithium, and hydride reagents.[5] We reasoned that diastereoselective reduction of oxazinyl 2-furylketone **1a** could give the carbinols (S)-**2a** or (R)-**2a**, from which optically active 2-furyldiol **4b** could be obtained after acidic hydrolysis followed by reduction. Also, ketone **1a** that can be considered as an extension of α-alkoxyketone imposes an interesting question as to the involvement of the furan oxygen in chelation. If the furan oxygen is involved in chelation, the diastereoselectivity in the reduction of **1a** is expected to be lower than in the case of **1b**.[6] In this paper we wish to report on the highly diastereoselective reduction of **1a** and rationalize this result with stereochemical models.

Table 1. Diastereoselectivities in the Reduction of Ketone **1a**

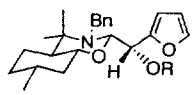
Reducing agents	Solvent	Temp. (℃)	(S)-**2a**	(R)-**2a**	de%[a]
$NaBH_4$	EtOH	0	98	2	96
$LiAlH_4$	THF	−78	90	10	80
$LiAlH_4$	ether	−78	98	2	96
L-Selectride®	THF	−78	98	2	96
L-Selectride®	ether	−78	98	2	96
n-Bu_4NBH_4	CH_2Cl_2	20	98	2	96
n-Bu_4NBH_4	THF	20	90	10	80
$LiAl(O$-t-$Bu)_3H$	THF	20	90	10	80
$LiAl(O$-t-$Bu)_3H$	ether	20	99	1	98
$LiAl(O$-t-$Bu)_3H$/ 15-crown-5 (2 eq.)	ether	20	99	1	98
$LiAl(O$-t-$Bu)_3H$/ TMEDA (10 eq.)	ether	20	98	2	96
$Zn(BH_4)_2$	ether	−78	98	2	96
dibal	toluene	−78	55	45	10

[a] The diastereomeric ratios were determined by the integration of C-2 proton signal of the ^{1}H-NMR spectra.

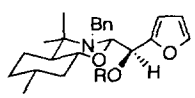
Ketone **1a**[7] was prepared by condensation (CH_2Cl_2, molecular sieve 3A, reflux, 2 days) of amino alcohol **3**[5] with 2-furylglyoxal hydrate[8] in 65% yield as colorless crystal, mp 82-83℃ and was reduced to give a mixture of (S)-**2a**[9] and (R)-**2a**, with the results shown in Table 1. The carbinol carbon formed in the $LiAl(O$-t-$Bu)_3H$ reduction was proven to have the (S)-configuration (*vide infra*). As one can see in Table 1, most reducing agents produced the (S)-isomer in high diastereomeric excess (de). However, diisobutylaluminum hydride (DIBAL) gave an almost equal mixture of two diastereomeric alcohols.



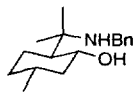
1a: R = 2-furyl
1b: R = phenyl



(S)-2a: R = H
(S)-2b: R = $SiPh_2$-*t*-Bu



(R)-2a: R =H



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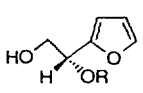

4a: R = $SiPh_2$-*t*-Bu
4b: R = H

Previously, high stereoselectivity observed in hydride reduction of 2-oxazinyl ketone **1** has been ascribed to the Cram's chelate model involving chelation to the oxygen rather than the nitrogen of the oxazine ring.[5] However, in the present case the reduction with n-Bu_4NBH_4 in CH_2Cl_2, which