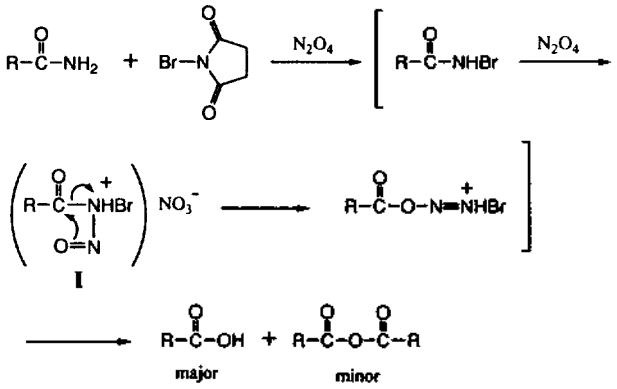
Table 1. Deamination of Amides by Dinitrogen Tetroxide with *N*-Bromosuccinimide

$$R\text{-}CONH_2 + NBS \xrightarrow[CH_3CN,\ r.t.,\ 20\ min]{} \xrightarrow[CH_3CN,\ -20\,^{\circ}C]{N_2O_4} R\text{-}CO_2H + (R\text{-}CO)_2O$$

1 **2**

Run	Amides	NBS (eq.)	N_2O_4 (eq.)	Time (h)	**1** (%)[a]	**2** (%)[a]
1	$PhCONH_2$	1.2	1.8	0.5	96	2
2	$PhCONH_2$	none	4.0	3.0	86	b
3	*p*-Me-$PhCONH_2$	1.2	1.8	0.5	92	6
4	*p*-Me-$PhCONH_2$	none	4.0	3.0	85	b
5	*p*-Cl-$PhCONH_2$	1.2	1.8	0.5	94	2
6	*p*-Cl-$PhCONH_2$	none	4.0	3.0	85	b
7	*o*-Me-$PhCONH_2$	1.2	1.8	0.5	94	trace
8	*p*-NO_2-$PhCONH_2$	1.2	2.0	0.5	93	4
9	*m*-NO_2-$PhCONH_2$	1.2	2.0	0.5	92	2
10	*p*-Br-$PhCONH_2$	1.2	1.8	0.5	95	trace
11	*p*-MeO-$PhCONH_2$	1.2	1.8	0.5	96	trace

[a] Isolated yields, [b] Not checked



Scheme 1.

and its anhydride which were separated by SiO_2 column chromatography to give benzoic acid (117 mg, 96%) and benzoic anhydride (2 mg, 2%).

The reaction appears to be initiated *via* bromination and then subsequent formation of transient nitronium bromide intermediate **I**.[12] Dinitrogen tetroxide is known to be in equilibrium with $NO^+ + NO_3^-$ ion in solution.[13] Nitrosation may occur rapidly on nitrogen to form a nitronium intermediate **I** which converts to the product of carboxylic acid. Rapid reaction in short time and the mild conditions may restrain formation of carboxylic acid anhydride from the carboxylic acid.

Although the reaction mechanism is not yet clear, this new interesting reaction is practical and may be available for the cleavage of C-N bond of amides. Additional research will be required to better understand the reaction mechanism.

This work was supported by the Basic Science Research Institute Program, Ministry of Education.

References

1. Challis, B. C.; Challis, J. A. *Comprehensive Organic Chemistry*, Sutherland ed.: ch. 9.9, 1979; p 957-1065.
2. Shahak, I.; Sasson, Y. *J. Am. Chem. Soc.* **1973**, *95*, 3440.
3. Lovejoy, D. J.; Vosper, A. J. *J. Am. Soc. A.* **1968**, 2325.
4. White, E. H.; Woodcock, D. J. In *The Chemistry of The Amino Group*; Patai, S. ed.; Interscience: London, ch. 8, 1968; p 407-497.
5. Olah, G. A.; Olah, J. A. *J. Org. Chem.* **1965**, *30*, 2386.
6. Kim, Y. H.; Kim, K.; Park, Y. J. *Tetrahedron Lett.* **1990**, *31*, 3893.
7. White, E. H. *J. Am. Chem. Soc.* **1954**, *76*, 4497; White, E. H. *J. Am. Chem. Soc.* **1958**, *77*, 6008.
8. de Boer, Th. J.; Backer, H. J. *Koninkl. Ned. Akad. Wetenschap. Proc.* **1954**, *55B*, 44.
9. Cooley, J. H.; Jacobs, P. T.; Khan, M. A.; Heasley, L.; Goodman, W. D. *J. Org. Chem.* **1965**, *30*, 3062.
10. De Christopher, P. J.; Adamek, J. P.; Lyon, G. D.; Galante, J. J.; Haffner, H. E.; Boggio, R. J.; Baumgarten, R. J. *J. Am. Chem. Soc.* **1949**, *91*, 2384.
11. Concentration of N_2O_4 in CCl_4 was determined by titration before using according to the following equation: $3N_2O_4 + 2H_2O \rightarrow 4HNO_3 + 2NO$: Gray, P.; Yoffe, A. D. *Quart. Rev.* **1955**, *9*, 376.
12. The possible intermediate **I** was detected by careful NMR and IR study, and TLC monitering of the reaction mixture. It was identified not to be *N*-bromosuccinimide by comparing their spectral data with those from authentic *N*-bromosuccinimide. The reaction mixture solution of benzamide and NBS in CD_3CN was taken for ^1H-NMR and TLC each other after 5, 10, 30 min and 1 h.
13. Augus, W. R.; Jones, R. W.; Phillips, G. O. *Nature* **1947**, *164*, 433; Clusius, K.; Vecchi, M. *Helv. Chim. Acta.* **1953**, *36*, 930.

Catalytic Enantioselective Reactions. Part 2.[1] A Comparison Study of Asymmetric Borane Reduction of Prochiral Ketones Catalyzed by Chiral Oxazaborolidines

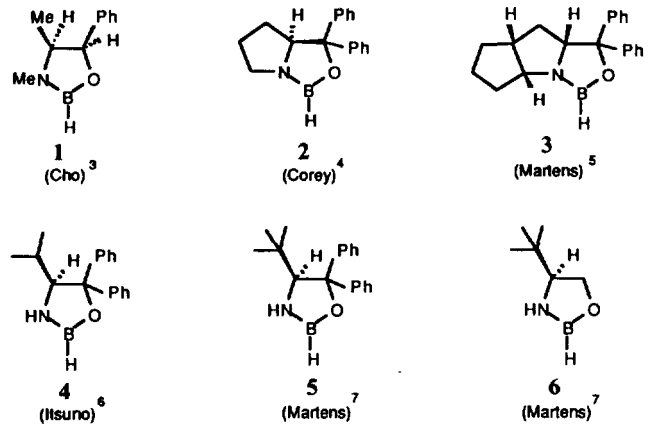
Byung Tae Cho*[†], Yu Sung Chun[†], Ch. Dauelsberg[‡], Sabine Wallbaum[‡], and Jürgen Martens[‡]

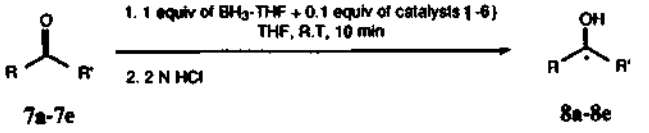
[†]*Department of Chemistry, Hallym University Chunchon 200-702*

[‡]*Fachbereich Chemie, Universität Oldenburg, Heerstraße 114-118, D-2900 Oldenburg i.O., Germany*

Received September 10, 1993

Recently much attention has been focused on the asymmetric reduction of prochiral ketones catalyzed by a variety of chiral oxazaborolidines.[2] However, the direct comparison study on the catalytic effectiveness of these oxazaborolidines





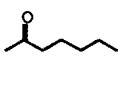
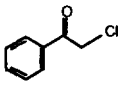
Scheme 1.

for the asymmetric reduction of ketones has not been accomplished. Such systematic comparison among catalysts would greatly assist synthetic organic chemists in selecting an appropriate catalyst for a desired transformation. We now wish to report such a comparative study by employing asymmetric borane reduction of the same ketones using a variety of chiral oxazaborolidines as catalysts.

The following chiral 1,3,2-oxazaborolidines **1-6** derived from (-)-ephedrine, natural and unnatural α-amino acids such as (S)-proline, (S)-valine, a bicyclic proline (1R, 3R, 5R)-2-azabicyclo[3.3.0]octan-3-carboxylic acid, and (S)-*tert*-leucine were selected (Scheme 1). And the prochiral ketones, such as acetophenone (**7a**) for aromatic ketones, 2-heptanone (**7b**) for unhindered aliphatic ketones, 3,3-dimethyl-2-butanone (**7c**) for hindered aliphatic ketones, α-tetralone (**7d**) for aromatic cycloalkanones, and 2-chloroacetophenone (**7e**) for α-haloketones were chosen as representative. We first collected the asymmetric reduction data available in the literatures for the representative ketones using the selected catalysts. And the catalytic asymmetric reduction, in case where the data were not available, were carried out carefully following the published procedures.

The chiral oxazaborolidine **1** was prepared from borane methyl sulfide and (1R, 2S)-(-)-ephedrine[3] and the others **2-6** were generated *in situ* from borane-THF and their precursors β-chiral amino alcohols by each of reported procedures.[4-7] Optical purities of the products alcohols (**8**) were determined by capillary GC analyses of MTPA esters[8] prepared by the reaction of the products alcohols with (R)-(-)-MTPA acid chloride[9]. Thus, the ketones **7** were treated with 1 equiv of borane-THF in the presence of 0.1 equiv of each catalyst **1-6** in THF at room temperature (*ca.* 28℃). All of the reductions examined were complete within 10 min to give the corresponding alcohols in 97-100% yields. The following general procedure is representative. To a solution of oxazaborolidines (0.1 equiv) and borane-THF (1 equiv) in THF was added slowly the selected ketones **7** in THF. After stirring for 10 min at room temperature, the reaction mixture was hydrolyzed with 2 N HCl. THF was removed *in vacuo* and the residue was extracted with diethyl ether. The extract was washed with brine and dried over anhydrous $MgSO_4$. The yields of products alcohols **8** were determined by GC analysis, isolated by bulb-to-bulb distillation and their optical purities were determined by the analytical methods as mentioned above. The results were summarized and compared in Table 1. For aromatic ketones, represented by acetophenone (**7a**), all of the catalysts tested afforded good enantioselectivities (61-97% ee). In particular, **2** was highly effective for the reduction to give **8a** of 97% ee. In contrast, for unhindered ketones, represented by 2-heptanone (**7b**), all of the catalysts examined provided low optical inductions (15-35% ee). For hindered aliphatic ketones, aromatic cycloalkanones, and α-halo ketones, represented by 3,3-dimethyl-2-butanone (**7c**), α-tetralone (**7d**), and 2-chloroacetophenone (**7e**), respectively, **2** was the most effective for the reductions to give the corresponding alcohols **8c-8e** with 89-97% ee. Further studies for the development of new chiral catalysts to improve optical yields in the reduction of unhindered aliphatic ketones are under investigation.

Table 1. Comparison of the Asymmetric Borane Reduction of Ketones **7a-7e** Catalyzed by Chiral Oxazaborolidines **1-6** in Tetrahydrofuran at Room Temperature[a]

Catalysts	% ee of products alcohols (**8a-8e**)				
	 **7a**	 **7b**	 **7c**	 **7d**	 **7e**
1	70, R[b]	15, R	59, R[b]	28, R	32, S
2	97, R[c]	34, R	92, R[c]	89, R[c]	97, S[c]
3	61, S[d]	19, S	19, S	7, S	69, R
4	65, R	27, R	43, R	38, R	68, R
5	89, R[e]	17, R	18, R	46, R	69, S
6	80, R[e]	35, R	68, R	18, R	25, S

[a]All of the reductions were carried out with ketones : catalysts : borane-THF (1 : 0.1 : 1) in THF, unless otherwise indicated. At present work, optical yields of the products alcohols were determined by capillary GC analyses of their MTPA esters. [b]Data taken from ref. 3. [c]Data taken from ref. 4. [d]By optical rotation of the product alcohol **8a** obtained by the presence of 1 mole% of 3 : ref. 5 [e]By optical rotation of **8a**: ref. 7.

Acknowledgement. We are grateful to the Organic Chemistry Research Center/KOSEF and Fonds der Chemischen Industrie and Degussa AG for financial support.

References

1. Part 1: see ref. 3.
2. For a recent review, see: (a) Singh, V. K. *Synthesis*, **1992**, 605; (b) Wallbum, S.; Martens, J. *Tetrahedron: Asymmetry* **1992**, *3*, 1475; (c) Deloux, A.; Srebnik, M. *Chem. Rev.* **1993**, *93*, 763.
3. Cho, B. T.; Chun, Y. S. *Tetrahedron: Asymmetry* **1992**, *3*, 1539.

4. Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551.
5. Wallbaum, S.; Martens, J. *Tetrahedron: Asymmetry* **1991**, *2*, 223.
6. Itsuno, S.; Nakano, M.; Miyazaki, K.; Masuda, H.; Itoh, K.; Hirao, A.; Nakahama, S. *J. Chem. Soc., Perkin Trans. I* **1985**, 2039. In this paper, a defined structure of the reagent was not reported, but the structure was apparent after Corey's work (ref. 4).
7. Behnen, W.; Dauelsberg, Ch.; Wallbaum, S.; Martens, J. *Synth. Commun.* **1992**, *22*, 214.
8. Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543; MTPA=α-methoxy-α-trifluoromethyl-phenylacetic acid.
9. Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

Photoadditions of *o*-Quinones to 1,4-Diphenyl-1,3-butadiene

Sung Sik Kim*, Young Hyun Yu, Dong Yeol Yoo, Sang Kyu Park, and Sang Chul Shim†

Department of Chemistry, Chonbuk National University, Chonju 560-756

†*Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701*

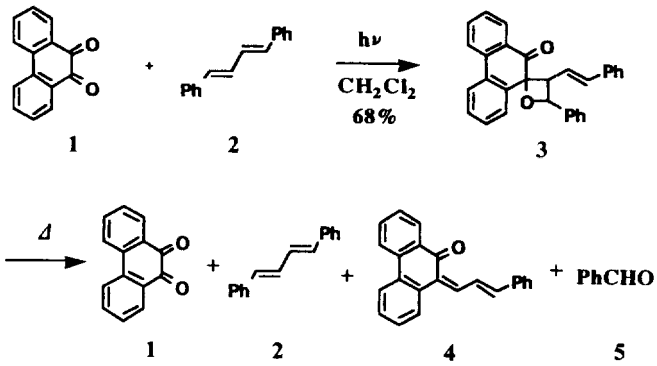
Received September 27, 1993

Quinones are an important class of compounds in industry, in organic synthesis, and in Nature.[1] Due to their various spectral properties, the photochemistry of quinones has been a subject of interest in many areas.[2-4] Phenanthrenequinone (PQ) **1** is known to react with substituted acetylenes to give 1,4-dioxenes or 1,3-dioxoles.[5] The photochemical reactions of PQ and olefins give rise to dioxenes or keto oxetanes.[6-8]

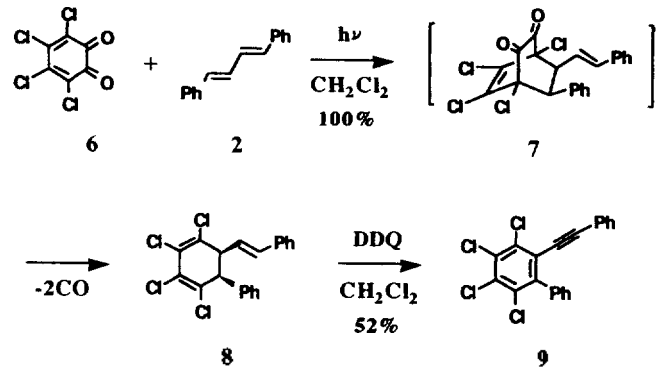
In connection with our investigation of the scope of these reactions, we examined the photochemistry of *o*-quinones and conjugated systems such as 1,4-diphenyl-1,3-butadiyne (DPBy) and *trans,trans*-1,4-diphenyl-1,3-butadiene (DPBe) **2**. Although no adduct was found in the photoreactions of PQ with diphenylacetylene and DPBy, a 1 : 1 adduct **3** was obtained in 68% yield when irradiated PQ **1** and DPBe **2** in dichloromethane.[9]

A solution of 150 mg (7.2×10^{-4} mol) of PQ **1** and 222 mg (1.08×10^{-3} mol) of DPBe **2** in 100 mL of dichloromethane was deoxygenated using nitrogen gas and irradiated with 350 nm UV light for 12 h. After evaporation of the solvent, the residue was chromatographed on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate as eluents. Elution with *n*-hexane afforded unreacted DPBe **2**. Elution with 2% ethyl acetate in *n*-hexane afforded 205 mg (68% based on PQ) of adduct **3**.

The structure of 1 : 1 adduct **3** was characterized by UV, IR, 400 MHz ^{1}H-NMR, ^{13}C-NMR, and mass spectra. ^{1}H-^{13}C correlation spectrum of **3** shows that the peaks at 134.3 ppm and 123.3 ppm in the ^{13}C dimension correspond to the vinyl protons (PhC<u>H</u>= and PhCH=C<u>H</u>-) in the ^{1}H dimension; the two methine ^{1}H resonances at 3.78 ppm and near 6.06 ppm[10] correspond to the two ^{13}C signals at 62.8 ppm and 81.2 ppm, respectively. **3** undergoes slow thermal dissociation at room temperature. Standing **3** at room temperature for 15 h gave rise to not only starting materials, PQ **1** and DPBe **2**, but also benzaldehyde **5** and its corresponding decomposition compound **4**. The three vinyl protons of **4** were observed at 6.85 ppm (d, J=16.12 Hz), 6.19 ppm (d, J=16.16 Hz), and 5.99 ppm (dd, J=16.16 and 16.12 Hz).



Scheme 1.



Scheme 2.

Refluxing a dichloromethane solution of tetrachloro-1,2-benzoquinone (*o*-TCBQ) **6** and DPBe **2** for 18 h gave rise to tetrachloro-1,3-cyclohexadiene derivative **8** in 99% yield.

Photochemical reaction of *o*-TCBQ **6** and DPBe **2** in dichloromethane with 350 nm UV light only for 2 h also afforded **8** quantitatively.[11] The stereochemistry of the *cis*-adduct **8** was rationalized by using the result of MMX data.[12] The magnitude of the coupling constant (J) between two adjacent CH bonds is depend directly on the dihedral angle between these two bonds, in which the magnitude is largest when the angle is 0° or 180°, and is smallest when the angle is 90°. ^3J of the *cis*-adduct **8** was 7.65 Hz.[11,12] The formation of **8** probably proceeds *via* [4+2] adduct **7**[13,14], which would be expected to undergo rapid photobisdecarbonylation,[13,14] ^{1}H-^{13}C correlation spectrum was also obtained to assign the exact positions of the carbon atoms of **8**.[15]

Refluxing a dichloromethane solution of **8** in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for 12 h gave rise to the oxidized product **9** in 52% yield.[16]

^{1}H-NMR spectrum of **9** shows that all the four proton sig-