attack the carbon at six position in **4** due to the bulkiness of the tert-butyl group. Thus compound **4** may be stable in tert-butyl alcohol. More detailed work is being under investigation

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14. When CD_3OD and DMSO-d_6 was completely removed under high vacuum, **4a** was recovered and confirmed.

Photocatalyzed Reduction of Esters by β-Naphthoxyboranes and Lithium tri-β-Naphthoxyborohydride

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On an expectation of changes in reactivities and selectivities of sodium borohydride and as a new attempt to reduce the functional groups that are not reduced under the normal conditions by sodium borohydride, the irradiation effect on borohydride reduction system was investigated[1]. The reduction of esters and ketones with sodium borohydride under uv irradiation showed remarkably different results from ordinary thermal reduction[2]. The quantum yields were larger in nonpolar solvents than in polar solvents. The reduction of cyclohexanecarboxylic acid esters with the pure (n, π^*) state as the lowest excited state was very much accelerated on photoexcitation. In our previous experiments, all the light was absorbed by carbonyl compounds. We, therefore, investigated the photo-enhanced reduction of esters by various reducing agents having a chromophore themselves and all the light was absorbed by the reducing agents not by carbonyl compounds.

In a typical experiment, an oven dried rubber-capped test tube was flushed with nitrogen and 1.2 mmol of lithium tri-β-naphthoxyborohydride in THF (1.6 m*l*) was introduced into the test tube and diluted with THF to 2.0 m*l*. The reduction was started by the addition of 0.3 mmol of cyclohexanecarboxylic acid ester in THF (1.0 m*l*). The final solution(3 m*l*) was 0.1 M cyclohexanecarboxylic acid ester and 0.4 M hydride. The mixture was irradiated in a merry-go-round for 3.0 h with 334 nm light through a filter solution at room temperature. After irradiation, 2 m*l* of the reaction mixture was transferred into a 5 m*l* volumetric flask and added 1 m*l* of 6N sulfuric acid to destroy the unreacted borohydride. After hydrogen gas evolution ceased, the solution was neutralized with concentrated aqueous sodium hydroxide solution and diluted to 5 m*l* with distilled water and the amount of alcohol produced was determined by gas chromatographic (GC) analysis. A blank solution (2 m*l*) was treated by the same procedure and analyzed by GC for a control. Quantum yields were determined utilizing tris(oxalato) ferrate actinometry and GC using Carbowax 20M 6'x1/8" column. The results are summarized in Table 1.

The reduction of cyclohexanecarboxylic acid esters with mono-β-naphthoxyborane in THF was carried out irradiating with 334 nm light. All the light was absorbed by the reducing agent itself. The reduction of most of the cyclohexanecarboxylic acid esters with di-β-naphthoxyborane, in particular, was very much accelerated on irradiation as shown in Table 1.

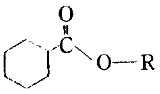
An important photochemical consequence by the change in molecular structure and electronic distribution on excitation is the drastic change of pK_a in S_1 and T_1 states[3]. The pK_a value of β-naphthol is 9, 3, and 8 in the S_0, S_1, and T_1 states, respectively. In general, the pK_a of the triplet state is remarkably close to that of the ground state while the excited singlet state possesses a substantially different pK_a from that of So and T_1 states[3].

The decreased reactivity of lithium tri-β-naphthoxyborohydride and the increased reactivity of β-naphthoxyboranes for the reduction of cyclohexanecarboxylic acid esters on irrandiation can be explained by the increased acidity of β-naphthoxy group in the singlet (π, π^*) excited state. Consequently β-naphthoxyborane is more readily coordinated to carbonyl oxygen atom of ester which is electron rich, and the hydride anion transfer from metal atom is decreased in the singlet excited state of lithium tri-β-naphthoxyborohydride. The results offer a new method and possibility to control the reducing power of borohydride by introducing new substituents which will change the acidity of acidic borohydride or the basicity of basic borohydride in the excited state.

When the reduction of cyclohexanecarboxylic acid esters with lithium tri-β-naphthoxyborohydride was carried out with 334 nm irradiation, phenyl and 4-tolyl cyclohexanecarboxylates gave guantum yeilds of 2.36 and 1.05 as shown in Table 1. But the reduction of most of the cyclohexanecarboxylic acid esters wat not accelerated on irradiation with 334 nm light but yields were decreased on irradiation due to the increased acidity of β-naphthoxy group in the (π, π*) singlet excited state. The ability of hydride anion transfer from metal atom is, therefore, decreased in the singlet excited state of lithium tri-β-naphthoxyborohydride.

In conclusion, the results offer a new method and possibility to control the reducing power of borohydrides by introducing appropriate light absorbing substituents into the borohydride followed by uv irradiation.

Table 1. Reduction of Cyclohexanecarboxylic Acid Esters with Light Absorbing Reducing Agents[a]

Reducing agents	R in 	Reduction(%)	
		Thermal	Photocatalyzed (Quantum yield)
Mono-β-naphthoxyborane	Phenyl	9.0	25.8 (0.66)
	2-tolyl	8.6	23.4 (0.58)
	3-tolyl	18.3	25.1 (0.27)
	4-tolyl	19.5	39.7 (0.79)
	2-chlorophenyl	12.2	12.2 (0.00)
	4-chlorophenyl	14.0	18.9 (0.19)
	4-methoxyphenyl	25.3	27.0 (0.07)
	methyl	47.3	59.1 (0.43)
Di-β-naphthoxyborane	phenyl	10.0	21.3 (0.45)
	2-tolyl	16.8	26.3 (0.37)
	3-tolyl	9.9	27.6 (0.60)
	4-tolyl	11.3	13.5 (0.08)
	2-chlorophenyl	2.4	10.2 (0.31)
	4-chlorophenyl	2.7	12.8 (0.40)
	4-methoxyphenyl	13.2	22.9 (0.38)
	methyl	30.5	38.5 (0.31)
Lithium tri-β-naphthoxyborohydride	phenyl	2.8	11.2 (2.36)
	2-tolyl	10.1	7.7 (0.00)
	3-tolyl	13.3	9.3 (0.00)
	4-tolyl	9.7	13.4 (1.05)
	2-chlorophenyl	28.4	23.3 (0.00)
	4-chlorophenyl	27.3	24.6 (0.00)
	4-methoxyphenyl	10.0	9.5 (0.00)
	methyl	27.0	24.7 (0.00)

[a] Irradiated for 3 h at 334 nm.

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Desulfurization of Thioamide Derivatives into Their Corresponding Amides Using Superoxide Anion ($O_2^{\overline{\cdot}}$)

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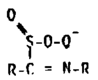
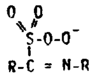
Considerable interest has recently been focused on the desulfurization of thiocarbonyl compounds using superoxide[1,2] and a related system of alkaline autoxidation[3] since oxidative desulfurization of thioamides[4,5] such as thiobarbiotal, ethionamide, or thiouracil has been known to be metabolized *in vivo* to give the corresponding carbonyl compounds without any evidence that an activated oxygen species like superoxide, which is distributed widely in living cells, is involved.

Our previous work on the oxidation of diaryl disulfide[6] and arylsulfonyl halides[7] to the corresponding sulfonates suggests that if peroxy-sulfur compounds *i.e.* peroxy-sulfinates or -sulfonates are formed, they may be useful intermediates in organic syntheses owing to their lability under alkaline conditions.

Superoxide anion is known to have quite strong basicity in the solution[8].



Peroxysulfinate



Peroxysulfonate

During the study of model metabolic reactions for desulfurization, we found that thioamide derivatives reacted with potassium superoxide in acetonitrile or tetrahydrofuran under mild conditions to form their corresponding amides together