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Photoreduction of Alkyl Halides by an NADH Model Compound. An Electron-Transfer Chain Mechanism

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Abstract: An NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), reduces alkyl halides such as benzyl bromide, *p*-cyanobenzyl bromide, and methyl iodide to yield the corresponding alkanes when only the absorption band of BNAH (λ_{max} 350 nm) is irradiated in the presence of pyridine. The quantum yields for the photoreduction of alkyl halides by BNAH exceed unity under the appropriate conditions. An electron-transfer chain mechanism has been presented on the basis of the inhibitory effect of a radical scavenger isopentyl nitrite and an electron acceptor *p*-dinitrobenzene on the rate of the photochemical reactions as well as the detailed analysis of the kinetics. The chain length and the propagation rate constant of the chain process have been determined. The rate constants of the electron-transfer reactions from the excited state of BNAH to alkyl halides determined from the fluorescence quenching of BNAH by alkyl halides have been consistent with those obtained from the kinetic analysis of the photochemical reactions. It is demonstrated that an electron transfer from the excited state of BNAH to alkyl halides is solely responsible for the photoinitiation step.

There has been considerable interest in the chemistry of 1,4-dihydronicotinic acid derivatives as the models of NADH which is one of the principal coenzymes for biochemical oxidation–reduction reactions.[1] Most model systems have been concerned with the thermal reduction of some activated substrates although the number of reducible substrates is limited in the thermal reactions.[1] On the other hand, the photochemistry of NADH model compounds[2–6] has merited a special attention to the possibility of increasing the number of reducible substrates. Especially, the discovery of a photochemical radical chain process for the reduction of bromotrichloromethane by an NADH model compound with high quantum yields ($\Phi = 7–80$)[3] has stimulated the studies on the photochemical reactions of NADH model compounds with various substrates.[4,5] Some attempts to enhance the rates of the photochemical reactions of NADH model compounds with use of sensitizers such as $Ru(2,2'\text{-bpy})_3Cl_2$[6] have also been reported.

The role of the excited state of an NADH model compound in the photochemical reactions, however, remains uncertain, because of a lack of knowledge on reactivities of the excited state of an NADH model compound. The chain process for the photochemical reactions of NADH model compounds has not been elucidated mechanistically either, since no satisfactory rate law to account for the postulated reaction mechanism has been derived.

In this paper, we wish to report that the specific excitation of the absorption band of an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), in MeCN containing alkyl halides (RX = benzyl bromide, *p*-cyanobenzyl bromide, and methyl iodide) results in the reduction of alkyl halides to the corresponding alkanes with quantum yields higher than unity under the appropriate conditions.[7] The role of the excited state of an NADH model compound (BNAH) in the photochemical reaction of BNAH with RX will be clarified by comparing the rate constant for the electron-transfer reaction of the excited state of BNAH with RX determined from the fluorescence quenching of BNAH by RX with that from the kinetic analysis of the photoreduction of RX by BNAH. The detailed reaction mechanism for the photoreduction of RX by BNAH will be presented on the basis of the rate law of the photochemical reaction as well as the inhibitory effects of a radical scavenger isopentyl nitrite and some electron acceptors.

Experimental Section

Materials. 1-Benzyl-1,4-dihydronicotinamide (BNAH) was prepared according to the literature,[8] and purified by recrystallization from ethanol. Benzyl bromide obtained from Wako Pure Chemicals was treated with concentrated H_2SO_4, water, 10% Na_2CO_3, and water. After the mixture was dried with $MgSO_4$, it was fractionally distilled in the dark under reduced pressure before use. Other electron acceptors (*p*-cyanobenzyl bromide, methyl iodide, *p*-dinitrobenzene, *m*-dinitrobenzene, nitrobenzene, diethyl fumarate, and dimethyl terephthalate) and a radical scavenger (isopentyl nitrite), also obtained commercially, were purified by the standard methods.[9] Potassium ferrioxalate used as an actinometer was prepared according to the literature,[10] and purified by recrystallization from hot water. Acetonitrile or pyridine used as a solvent was purified and dehydrated with calcium hydride by the standard procedure.[9]

Photochemical Reactions of BNAH with Alkyl Halides. Typically, a purified sample of benzyl bromide (0.84 mmol) was added to a Schlenk tube which contained an MeCN (1 cm^3) solution of BNAH (4.67×10^{-2} mmol) and pyridine (0.17 mmol). The Schlenk tube is equipped with a side arm fused to a square quartz cuvette (0.5, 1, or 10 mm i.d.). After the reactant solution in the tube was thoroughly degassed in vacuum by the successive freez–pump–thaw cycles, the solution was transferred to the quartz cuvette, which was then irradiated for a few hours with the visible light from a Ushio Model UI-501 Xenon lamp through a Toshiba glass filter O-36 transmitting light of $\lambda > 360$ nm. The rate of the photochemical reactions was measured from the decay of the absorption due to BNAH (λ_{max} 350 nm, ϵ 6.00×10^4 mol^{-1} dm^2)[11] by using a Union SM-401 spectrophotometer. Without the irradiation, the BNAH absorption has not been changed by the addition of purified benzyl bromide,

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Table I. Yields of the Products in the Photoreduction of Benzyl Bromide, *p*-Cyanobenzyl Bromide, and Methyl Iodide by BNAH under Irradiation of Light of λ >360 nm[a]

mmol of BNAH	mmol of $PhCH_2Br$	mmol of pyridine	condition	time, h	conv. of BNAH, %	yields of products, %	
						$PhCH_3$	PhC_2H_4Ph
5.60×10^{-2}	5.04[b]	0	degassed	2.6	91.3	1.7	2.1
4.67×10^{-3}	8.44×10^{-1}	4.95×10^{-3}	degassed	4.2	92.2	21.7	10.0
4.67×10^{-2}	8.44×10^{-1}	4.70×10^{-2}	degassed	2.5	80.1	52.0	3.4
1.64×10^{-2}	8.44×10^{-1}	7.42×10^{-2}	degassed	2.6	87.1	80.0	3.9
4.67×10^{-2}	8.44×10^{-1}	1.24×10^{-1}	degassed	2.6	78.6	72.9	2.7
						PhCHO	$PhCH_2OH$
4.67×10^{-2}	8.44×10^{-1}	1.24×10^{-1}	O_2[c]	3.6	74.7	22.0	23.2
9.34×10^{-2}	8.44×10^{-1}	2.48×10^{-1}	O_2[c]	7.2	62.9	11.9	12.7
	mmol of CH_3I					CH_4	C_2H_6
4.67×10^{-3}	8.05×10^{-1}	1.24×10^{-2}	N_2[d]	5.2	57.0	27.8	trace
4.67×10^{-3}	8.05×10^{-1}	2.48×10^{-2}	N_2[d]	5.0	50.7	24.2	trace
	mmol of *p*-$CNPhCH_2Br$					*p*-$CNPhCH_3$	
4.67×10^{-3}	8.44×10^{-1}	1.24×10^{-1}	degassed	2.5	74.0	66.3	

[a] In 1 cm³ of MeCN unless otherwise noted. [b] In 6 cm³ of MeCN. [c] Under an oxygen atmospheric pressure. [d] Under a nitrogen atmospheric pressure.

although the addition of unpurified benzyl bromide has caused the decrease of the BNAH absorption without the irradiation probably because of the adventitious radical chain reaction by impurities. The photochemical reaction of BNAH with benzyl bromide under an atmospheric pressure of oxygen also was carried out in a similar manner by introducing oxygen into the Schlenk tube after degassing the system.

The photochemical reaction of BNAH with *p*-cyanobenzyl bromide under a degassed condition was carried out by the same procedure as described above, whereas the reaction with methyl iodide was performed under an atmospheric pressure of nitrogen. All the resulting products were analyzed by GLC.

Quantum-Yield Determinations. A standard actinometer (potassium ferrioxalate)[10] was used for the quantum-yield determinations on the photochemical reactions of BNAH with alkyl halides. The quantum yield was determined in the region of visible light through the filter transmitting light of λ >360 nm, since the use of monochromatized light was too weak to measure the rate of the photochemical reactions accurately. Thus, the actinometry experiments were carried out at the same incident light intensity by the use of the same filter as that for the photochemical experiments of BNAH. Since the light absorption by the actinometer or BNAH is not complete in the longer wavelength region depending on the concentration, the fraction of light absorbed by the actinometer or BNAH must be considered explicitly. The amount of ferrous ions [Fe^{2+}] formed in the irradiated solution of the actinometer through the filter is then given by eq 1, where C is the proportional

$$[\mathrm{Fe}^{2+}] = C\Phi_0 t \int_0^\infty \chi(\lambda)F(\lambda)[1 - \exp(-2.303A_\lambda^0)]\,\mathrm{d}\lambda \qquad (1)$$

constant between the absolute light intensity absorbed by the actinometer and the relative value, Φ_0 is the quantum yield for the actinometer taken as 1.15 from the literature,[10] t is the irradiation time, $\chi(\lambda)$ is the relative emitting light intensity at the wavelength λ determined by using rhodamine 6G as a standard, $F(\lambda)$ is the wavelength dependence of the transmitting efficiency of the filter, and A_λ^0 is the absorbance of the actinometer at the wavelength λ. Similarly, the quantum yield Φ for the photochemical reaction of BNAH is given by eq 2, where Δ[BNAH] is

$$\Phi = \Delta[\mathrm{BNAH}] \Big/ \left(Ct \int_0^\infty \chi(\lambda)F(\lambda)[1 - \exp(-2.303A_\lambda)]\,\mathrm{d}\lambda\right) \qquad (2)$$

the amount of BNAH consumed by the photochemical reaction with an alkyl halide and A_λ is the absorbance of BNAH at the wavelength λ.

The value of the proportional constant C between the absolute and relative light intensity absorbed by the actinometer and BNAH in eq 1 and 2, respectively, was determined from the actinometry experiments by substituting [Fe^{2+}], Φ_0, t, and the integral term that was calculated by the numerical integration, into eq 1. When the C value thus obtained was used, the quantum yield Φ for the photochemical reaction of BNAH with benzyl bromide or *p*-cyanobenzyl bromide has been determined from eq 2, where the initial rate for the photochemical reaction ($\Delta[\mathrm{BNAH}]/t$) was used so as to avoid the decrease of the fraction of the absorbed light intensity with a decreasing in the concentration of BNAH.

Fluorescence-Quenching Experiments. Fluorescence measurements were carried out on a Hitachi 650-10S fluorescence spectrophotometer. The fluorescence quantum yield of BNAH upon excitation of the absorption maximum of BNAH (350 nm) in MeCN has been determined as 0.11 by using fluorescein in 0.1 N NaOH as a standard[12] in the following manner. The fluorescence spectra of both BNAH and the standard were measured at various concentrations under exactly the same instrumental conditions. The spectra were corrected and plotted on an energy scale, and the slopes for the areas vs. the concentrations were determined for both BNAH and the standard. The ratio of the slopes between BNAH and the standard was taken as the ratio of the quantum yields. The fluorescence quantum yield of the standard with 350-nm excitation was adopted as 0.84 from the literature[12] value with a similar excitation (366.5 nm).

Quenching experiments of the BNAH fluorescence were carried out by using the alkyl halides as quenchers. Relative fluorescence intensities of BNAH at 440 nm were measured for MeCN solutions containing BNAH and a quencher at various concentrations. The absorption band dut to BNAH was not changed by the addition of a quencher with high concentrations (>1 × 10^{-1} M). There has been no change in the shape but rather the intensity of the fluorescence spectrum by the addition of the alkyl halides. The Stern–Volmer relationship (eq 3) was obtained

$$\Phi_f^0/\Phi_f = 1 + K_q[\mathrm{Q}] \qquad (3)$$

between the ratio of the fluorescence quantum yields in the absence and presence of a quencher Φ_f^0/Φ_f and the quencher concentration [Q]. The quenching rate constant k_q was obtained from the quenching constant K_q and the fluorescence lifetime τ (0.76 ns)[11] by eq 4.

$$k_q = K_q\tau^{-1} \qquad (4)$$

Results

Products of Photoreduction. The electronic-absorption spectrum of BNAH in MeCN shows the lowest energy band at 350 nm. Benzyl bromide, *p*-cyanobenzyl bromide, and methyl iodide also exhibit no absorption band in the visible region. Since there has appeared no new band in the visible spectra of a mixture of alkyl halide and BNAH due to the complex formation between them, the BNAH band was specifically excited by using a Xenon lamp with a filter transmitting light of λ >360 nm. Although no reaction has occurred between BNAH and benzyl bromide in the dark, irradiation of a degassed MeCN solution containing BNAH (4.67 × 10^{-2} mmol) and benzyl bromide (8.44 × 10^{-1} mmol) together with pyridine (1.24 × 10^{-1} mmol) for 2.6 h has resulted in the consumption of 79% BNAH to yield toluene (73% on the basis of the initial amount of BNAH) as the main product (eq 5) and a small amount of 1,2-diphenylethane. *p*-Cyanobenzyl bromide and methyl iodide also were reduced photochemically by BNAH under degassed conditions in the presence of pyridine to yield *p*-cyanotoluene and methane as the main products, respectively. Yields of the photoproducts under various conditions are listed in Table I.

$$\mathrm{BNAH} + \mathrm{PhCH_2Br} \xrightarrow[\text{MeCN/pyridine}]{h\nu\ (>360\ \text{nm})} \mathrm{BNA^+} + \mathrm{Br^-} + \mathrm{PhCH_3} \qquad (5)$$

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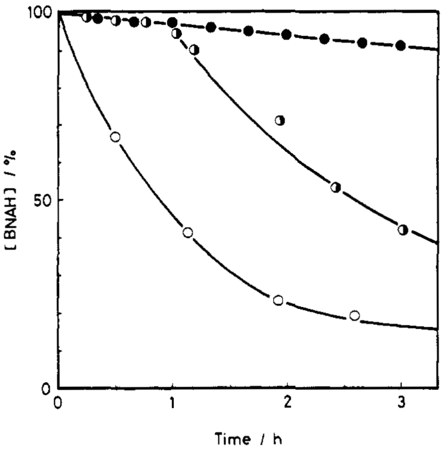

Figure 1. Inhibition of the photochemical reaction of BNAH (4.21×10^{-2} M) with benzyl bromide (7.60×10^{-1} M) in MeCN containing pyridine (1.11×10^{-1} M) with $In = 3.55 \times 10^{-6}$ einstein dm^{-3} s^{-1}: (○) no inhibitor; (●) 6.64×10^{-2} M isopentyl nitrite; (◑) 1.34×10^{-3} M isopentyl nitrite.

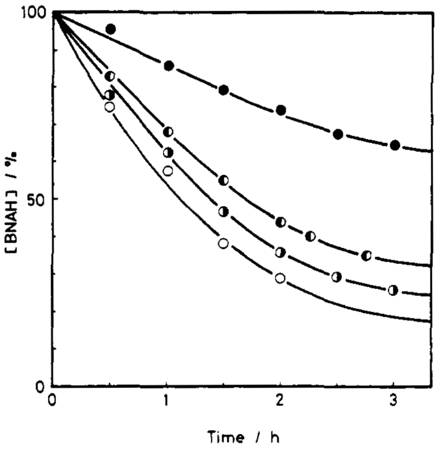

Figure 2. Retarding effect of electron acceptors on the photochemical reaction of BNAH (8.42×10^{-3} M) with benzyl bromide (7.60×10^{-1} M) in MeCN containing pyridine (1.11×10^{-1} M) with $In = 9.67 \times 10^{-7}$ einstein dm^{-3} s^{-1}; (○) no acceptor; (●) 1.34×10^{-3} M *p*-dinitrobenzene; (◐) 1.34×10^{-3} M *m*-dinitrobenzene; (◑) 1.34×10^{-3} M nitrobenzene.

In the absence of pyridine, the yield of toluene in the photochemical reaction of BNAH with benzyl bromide is significantly lower than that in the presence of pyridine with approximately the same conversion of BNAH (Table I). Thus, the presence of pyridine seems to be essential for obtaining a high yield of toluene in the photoreduction of benzyl bromide by BNAH.

When the photochemical reaction of BNAH with benzyl bromide was carried out in the presence of an atmospheric pressure of oxygen under the same conditions otherwise as the reaction in eq 5, the formation of toluene was completely suppressed and instead equimolar amounts of benzyl alcohol and benzaldehyde were formed (Table I). In the absence of BNAH, however, oxygen has not converted benzyl bromide into benzyl alcohol and benzaldehyde by the irradiation of light of λ >360 nm.

Effects of a Radical Scavenger and Electron Acceptors on the Photochemical Reaction of BNAH with Benzyl Bromide. Rates of the photochemical reaction of BNAH (4.21×10^{-2} M) with benzyl bromide (7.60×10^{-1} M) under degassed conditions were determined from the decay of the absorption band due to BNAH in the absence or presence of isopentyl nitrite, which is known as an efficient radical scavenger.[13] Figure 1 clearly demonstrates the inhibitory effect of isopentyl nitrite on the photochemical reaction of BNAH with benzyl bromide in the presence of pyridine. Thus, the addition of 6.64×10^{-2} M isopentyl nitrite suppresses the photochemical reaction significantly as shown in Figure 1. The addition of a much smaller amount of isopentyl nitrite (1.34×10^{-3} M) similarly suppresses the occurrence of the photochemical reaction for the initial first hour, which is considered as the induction period, followed by the rapid consumption of BNAH with approximately the same rate as that in the absence of isopentyl nitrite (Figure 1). This behavior is taken as evidence for a radical chain reaction.

The addition of *p*-dinitrobenzene which is a typical electron acceptor[14] also retards the photochemical reaction of BNAH with benzyl bromide in the presence of pyridine as shown in Figure 2. The retarding effect was also observed by the addition of other electron acceptors with the same concentration (1.34×10^{-3} M) as *p*-dinitrobenzene (Figure 2), and the magnitude of the retarding effect decreased in the order *p*-dinitrobenzene > *m*-dinitrobenzene > nitrobenzene, in agreement with the order of the ability of the electron acceptors.[15]

Quantum Yields. Quantum yields Φ for the photochemical reaction of BNAH with benzyl bromide or *p*-cyanobenzyl bromide in the presence of pyridine on the irradiation of light of λ >360 nm are presented in Table II. The Φ value for the BNAH–benzyl bromide system increases with an increase in the concentration of BNAH or benzyl bromide. Thus, a quantum yield higher than unity (Φ = 1.61) is achieved for a mixture of 8.42×10^{-3} M BNAH and 7.60×10^{-1} M benzyl bromide with the absorbed light intensity 9.67×10^{-7} einstein dm^{-3} s^{-1}. When *p*-cyanobenzyl bromide is used in place of benzyl bromide, the quantum yield increases by a factor of 4–6 under the same conditions as used with benzyl bromide (Table II).

Table II. *Quantum Yields (Φ) of the Photoreduction of Benzyl Bromide and p-Cyanobenzyl Bromide by BNAH in MeCN Containing 1.11×10^{-1} M Pyridine under Irradiation of Light of λ >360 nm*

[BNAH], M	[PhCH$_2$Br], M	*In*,[a] einstein dm^{-3} s^{-1}	Φ
8.42×10^{-3}	7.60×10^{-1}	9.67×10^{-7}	1.61
4.21×10^{-3}	7.60×10^{-1}	9.67×10^{-7}	0.65
4.21×10^{-4}	7.60×10^{-1}	4.84×10^{-7}	0.12
4.21×10^{-4}	3.98×10^{-1}	4.84×10^{-7}	0.11
4.21×10^{-4}	1.64×10^{-1}	4.84×10^{-7}	0.084
4.21×10^{-4}	8.26×10^{-2}	4.84×10^{-7}	0.069
4.21×10^{-4}	5.81×10^{-2}	4.84×10^{-7}	0.056
	[*p*-CNPhCH$_2$Br], M		
4.21×10^{-4}	7.60×10^{-1}	4.84×10^{-7}	0.53
4.21×10^{-4}	1.64×10^{-1}	4.84×10^{-7}	0.43
4.21×10^{-4}	8.26×10^{-2}	4.84×10^{-7}	0.38
4.21×10^{-4}	5.81×10^{-2}	4.84×10^{-7}	0.33

[a] Absorbed light intensity by BNAH.

Fluorescence Quenching by Electron Acceptors. The excitation of the absorption band (350 nm) of an MeCN solution of BNAH results in fluorescence (λ_{max} 443 nm, $h\nu_f = 2.80$ eV, $\tau = 0.76$ ns).[11] The fluorescence quantum yield Φ_f^0 of BNAH in MeCN with 350-nm excitation has been determined as 0.11 by using fluorescein as a standard[12] (see Experimental Section). The BNAH fluorescence was quenched by the alkyl halides (benzyl bromide, *p*-cyanobenzyl bromide, and methyl iodide) without a change in the shape of the fluorescence spectrum. Quenching rate constants k_q for the alkyl halides have been determined by the Stern–Volmer plots (eq 4). The result is listed in Table III, which also involves the k_q values of the BNAH fluorescence with other quenchers[11] and the reduction potentials of the quenchers.[11,16]

The quenching rate constant for *p*-cyanobenzyl bromide is close to the diffusion rate constant 2×10^{10} M^{-1} s^{-1},[17] and decreases

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(15) See the reduction potentials in Table III.

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Table III. Quenching Rate Constants (k_q) of the BNAH Fluorescence and Reduction Potentials (E^0_{red}) of Electron Acceptors

acceptor	E^0_{red} vs. SCE, V	k_q,[a] M^{-1} s^{-1}
p-dinitrobenzene	−0.69[b]	
m-dinitrobenzene	−0.90[b]	
nitrobenzene	−1.15[b]	
diethyl fumarate[c]	−1.50	1.6×10^{10} (1.3×10^{10})
dimethyl terephthalate[c]	−1.78	1.7×10^{10} (1.6×10^{10})
1-cyanonaphthalene[c]	−1.96	1.6×10^{10}
acetophenone[c]	−2.10	9.4×10^{9}
p-cyanobenzyl bromide	*d*	1.3×10^{10} (1.1×10^{10})
benzyl bromide	*d*	4.9×10^{9} (4.9×10^{9})
methyl iodide	*d*	1.4×10^{9} (1.5×10^{9})

[a] In MeCN (the values in parentheses are those in pyridine or in MeCN containing 1.22×10^{-1} M pyridine). [b] Taken from ref 16. [c] Taken from ref 11. [d] The electrochemical reduction is irreversible.

in the order *p*-cyanobenzyl bromide > benzyl bromide > methyl iodide, in accordance with the order of the rate of the photochemical reactions of BNAH. Other electron acceptors whose reduction potentials are more positive than 1-cyanonaphthalene (E^0_{red} = −1.96 V vs. SCE) also give rate constants close to diffusion limited. Thus, the k_q values for *p*-dinitrobenzene, *m*-dinitrobenzene, and nitrobenzene (the reduction potentials are more positive than that of 1-cyanonaphthalene as shown in Table III) are also expected to be diffusion limited, although they have not been determined because of the overlap of the electronic spectra with that of BNAH.

The effect of pyridine on the quenching rate constants has also been examined (the values in parentheses in Table III). It is shown that pyridine has no effect on the quenching rates of BNAH fluorescence by the electron acceptors.

Discussion

Electron-Transfer Initiation. The efficient inhibition of photochemical reactions by a radical scavenger (Figure 1) as well as the quantum yield higher than unity (Table II) unambiguously indicate that the photoreduction of benzyl bromide proceeds via a radical-chain process. As such it necessarily involves the initiation, propagation, and termination steps. We first focus on the initiation step of the chain process.

The excited state of BNAH acts as an excellent electron donor that can transfer an electron to various electron acceptors as shown in Table III. One-electron transfer to alkyl halides such as benzyl bromide is known to result in the facile fission of the carbon–halogen bond, yielding alkyl radicals.[18-20] It is therefore suggested that benzyl radicals may be formed in the photoinitiation step by the following sequence

initiation

$$\mathrm{BNAH} \xrightarrow{h\nu\ (>360\ \mathrm{nm})} \mathrm{BNAH}^* \tag{6}$$

$$\mathrm{BNAH}^* + \mathrm{PhCH_2Br} \xrightarrow{k_q} \mathrm{BNAH}^{+}\cdot + \mathrm{PhCH_2Br}^{-}\cdot \tag{7}$$

$$\mathrm{PhCH_2Br}^{-}\cdot \xrightarrow{\text{fast}} \mathrm{PhCH_2}\cdot + \mathrm{Br}^- \tag{8}$$

The formation of benzyl radicals in the photochemical reaction of BNAH with benzyl bromide is supported by the detection of the coupling product of benzyl radicals (eq 9) as shown in Table

$$2\mathrm{PhCH_2}\cdot \rightarrow \mathrm{PhCH_2CH_2Ph} \tag{9}$$

I. In the presence of oxygen, benzyl radicals are trapped by oxygen to yield benzylperoxyl radicals (eq 10) which are known to undergo

$$\mathrm{PhCH_2}\cdot + \mathrm{O_2} \rightarrow \mathrm{PhCH_2O_2}\cdot \tag{10}$$

a bimolecular reaction, producing equimolar amounts of benzyl alcohol and benzaldehyde as well as oxygen (eq 11).[21] Thus, the

$$2\mathrm{PhCH_2O_2}\cdot \rightarrow \mathrm{PhCH_2OH} + \mathrm{PhCHO} + \mathrm{O_2} \tag{11}$$

formation of equimolar amounts of benzyl alcohol and benzaldehyde in the photochemical reaction of BNAH with benzyl bromide under oxygen atmosphere (Table I) also confirms the involvement of benzyl radicals in the chain process.

If it is assumed that the electron transfer from the excited-state BNAH* to benzyl bromide (eq 7) may solely be responsible for the photoinitiation step, the initiation rate R_i is equal to $In(\Phi_f^0 - \Phi_f)$, in which In is the light intensity absorbed by BNAH, Φ_f^0 and Φ_f are the fluorescence quantum yield of BNAH in the absence and presence of benzyl bromide, respectively, and then expressed by eq 12 using eq 3 and 4, where Φ_f^0 has been deter-

$$R_i = In\ \Phi_f^0 \frac{k_q\tau[\mathrm{PhCH_2Br}]}{1 + k_q\tau[\mathrm{PhCH_2Br}]} \tag{12}$$

mined as 0.11 (see Experimental Section) and τ is the fluorescence lifetime (0.76 ns).[11] The validity of eq 12 is supported by the inhibition experiments shown in Figure 1 as follows. The initiation rate R_i is determined as the rate of the photochemical reaction in the presence of an excess amount of the radical scavenger (isopentyl nitrite), i.e., 3.6×10^{-7} M s^{-1}. Essentially the same R_i value 3.7×10^{-7} M s^{-1} is obtained from the induction time (1 h) in Figure 1, assuming that one molecule of isopentyl nitrite traps completely one molecule of benzyl radical.[22] It should be noted that the presence of the radical scavenger isopentyl nitrite does not affect the initiation rate R_i since isopentyl nitrite has not quenched the BNAH fluorescence under the experimental conditions in Figure 1. The initiation rate R_i thus determined by the inhibition experiments shows a reasonable agreement with the R_i value (2.9×10^{-7} M s^{-1}) which is evaluated from eq 12, when the experimental errors (±20%) in both determinations are taken into account. Thus, it is concluded that the photoinitiation step is the electron transfer from the excited-state BNAH* to benzyl bromide (eq 7), followed by the fast formation of benzyl radical (eq 8).

The reduction of the yield of toluene in the absence of pyridine also is consistent with the formation of $\mathrm{BNAH}^{+}\cdot$ as a result of the electron transfer from BNAH* to benzyl bromide (eq 7), since $\mathrm{BNAH}^{+}\cdot$ is known to undergo disproportionation (eq 13),[23] and

$$2\mathrm{BNAH}^{+}\cdot \rightarrow \mathrm{BNA}^+ + (\mathrm{BNAH})\mathrm{H}^+ \tag{13}$$

the resulting protonated species $(\mathrm{BNAH})\mathrm{H}^+$ causes the catalytic decomposition of BNAH.[24] A similar decrease of yields of the product in the absence of pyridine has been reported for the photoreduction of diethyl fumarate by BNAH, where the role of pyridine is suggested to increase the reaction rate by solvation to BNAH*.[3a] In the present study, however, such a suggestion is disregarded, since pyridine has no effect on the rate constant for electron-transfer reactions between BNAH* and electron acceptors (Table III). Thus, the role of pyridine in the photoreduction of benzyl bromide by BNAH is considered to abstract the proton of $(\mathrm{BNAH})\mathrm{H}^+$ (eq 14).

$$(\mathrm{BNAH})\mathrm{H}^+ + \mathrm{py} \rightarrow \mathrm{BNAH} + \mathrm{pyH}^+ \tag{14}$$

Propagation Step. The quantum yields higher than unity (Table III), and the inhibition by a radical scavenger (isopentyl nitrite)

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and a strong electron acceptor (*p*-dinitrobenzene) have been well adopted as criteria[25] for assigning the electron-transfer chain (ETC) mechanism, in which single electron transfer plays important roles in both the initiation and propagation steps. Best known among ETC reactions is the $S_{RN}1$ reaction,[14,25-27] which is given in generalized notation in Scheme I. This mechanism

Scheme I

$$RX^{-}\cdot \rightarrow R\cdot + X^{-} \tag{15}$$

$$R\cdot + Y^{-} \rightarrow RY^{-}\cdot \tag{16}$$

$$RY^{-}\cdot + RX \rightarrow RY + RX^{-}\cdot \tag{17}$$

involves three types of reactive intermediates: radicals R· and radical anions $RX^{-}\cdot$ and $RY^{-}\cdot$. The radical anion $RX^{-}\cdot$ fragments to form radical R· and anion X^{-} (eq 15). The radical R· combines covalently with nucleophile Y^{-} to form radical anion $RY^{-}\cdot$ (eq 16) which does not fragment. Electron transfer from $RY^{-}\cdot$ to a substrate RX yields the product RY with regeneration of $RX^{-}\cdot$ (eq 17).

In the present case, however, the neutral species BNAH, which is considered as a hydrogen donor, is involved instead of the nucleophile anion Y^{-}. Thus, the chain propagation step in the photoreduction of benzyl bromide by BNAH is suggested as eq 18 and 19, where benzyl radicals formed in the initiation step (eq 7 and 8) abstract hydrogen from BNAH to yield a product $PhCH_3$ and a radical intermediate BNA· (eq 18). Electron transfer from BNA· to benzyl bromide may occur readily because of the low oxidation potential of BNA· (−1.2 V vs. SCE),[28] yielding BNA^+ and $PhCH_2Br^{-}\cdot$ (eq 19) which fragments to regenerate benzyl radical (eq 8). In fact, benzyl bromide is known to be reduced electrochemically at the reduction potential of BNA·.[29]

propagation

$$PhCH_2\cdot + BNAH \xrightarrow{k_p} PhCH_3 + BNA\cdot \tag{18}$$

$$BNA\cdot + PhCH_2Br \xrightarrow{k_p'} BNA^{+} + PhCH_2Br^{-}\cdot \tag{19}$$

The retarding effect of an electron acceptor *p*-dinitrobenzene on the photochemical reaction of BNAH with benzyl bromide (Figure 2) can be understood as the result of electron-transfer quenching of BNA· by *p*-dinitrobenzene (eq 20) in competition

$$BNA\cdot + p\text{-}(NO_2)_2C_6H_4 \rightarrow BNA^{+} + p\text{-}(NO_2)_2C_6H_4^{-}\cdot \tag{20}$$

with the reaction with benzyl bromide (eq 19), the former of which interrupts the chain process. The rate constant for the electron-transfer quenching is expected to decrease in the order *p*-dinitrobenzene > *m*-dinitrobenzene > nitrobenzene on the basis of the reduction potentials of the acceptors (Table III). This order is tantamount to the retarding effect of electron acceptors on the photochemical reactions (Figure 2). It should be noted that the effect of electron acceptors on the electron-transfer initiation process (eq 7) is negligible under the experimental conditions in Figure 2, where the concentration of the acceptors is 570 times smaller than that of benzyl bromide, since the rate of electron-transfer reactions of BNAH* with the electron acceptors is much less than that with benzyl bromide.[30]

Table IV. Chain Length for the Photochemical Chain Reaction of BNAH with Benzyl Bromide or *p*-Cyanobenzyl Bromide in MeCN[a]

[BNAH], M	$[PhCH_2Br]$, M	r,[b] M s^{-1}.	R_i,[c] M s^{-1}	chain length (r/R_i)
8.42×10^{-3}	7.60×10^{-1}	1.56×10^{-6}	7.84×10^{-8}	19.9
4.21×10^{-3}	7.60×10^{-1}	6.26×10^{-7}	7.84×10^{-8}	8.0
4.21×10^{-4}	7.60×10^{-1}	6.00×10^{-8}	3.92×10^{-8}	1.5
4.21×10^{-4}	3.98×10^{-1}	5.49×10^{-8}	3.17×10^{-8}	1.7
4.21×10^{-4}	1.64×10^{-1}	4.04×10^{-8}	2.01×10^{-8}	2.0
4.21×10^{-4}	8.26×10^{-2}	3.32×10^{-8}	1.24×10^{-8}	2.7
4.21×10^{-4}	5.81×10^{-2}	2.73×10^{-8}	9.40×10^{-9}	2.9
	[*p*-$CNPhCH_2Br$], M			
4.21×10^{-4}	7.60×10^{-1}	2.56×10^{-7}	4.70×10^{-8}	5.5
4.21×10^{-4}	1.64×10^{-1}	2.08×10^{-7}	3.31×10^{-8}	6.3
4.21×10^{-4}	8.26×10^{-2}	1.86×10^{-7}	2.41×10^{-8}	7.7
4.21×10^{-4}	5.81×10^{-2}	1.59×10^{-7}	1.96×10^{-8}	8.1

[a] Containing 1.11×10^{-1} M pyridine. [b] Initial rate of the disappearance of BNAH. [c] Initial rate of the initiation step evaluated from eq 12.

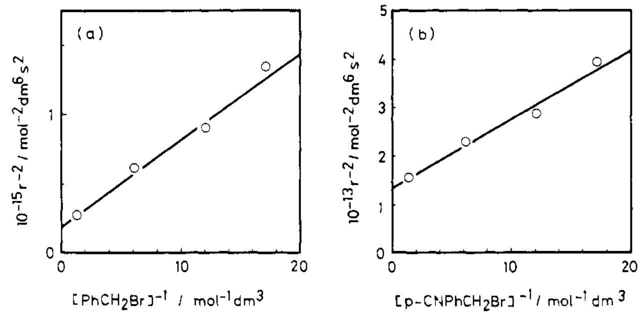

Figure 3. Plots of r^{-2} as a function of (a) $[PhCH_2Br]^{-1}$ and (b) $[p\text{-}CNPhCH_2Br]^{-1}$ for the photochemical reactions of BNAH with benzyl bromide and *p*-cyanobenzyl bromide in MeCN containing 1.11×10^{-1} M pyridine, respectively; see eq 23 in text.

The chain length for the photochemical reaction of BNAH with benzyl bromide or *p*-cyanobenzyl bromide is calculated from the ratio of the rate of the photochemical reaction to the initiation rate R_i evaluated from eq 12 under various conditions, as listed in Table IV. The maximum chain length (20) is achieved for 8.42×10^{-3} M BNAH and 7.60×10^{-1} M benzyl bromide in the presence of 1.11×10^{-1} M pyridine.

Kinetics. The proposed chain mechanism for the photoreduction of benzyl bromide by BNAH is further confirmed by the kinetics. The kinetic formulation depends on the mode of the termination step. It has been found that the termination through the bimolecular reaction of benzyl radicals (eq 21) can account for the kinetic results in the following manner.

termination

$$2PhCH_2\cdot \xrightarrow{k_t} PhCH_2CH_2Ph \tag{21}$$

By applying the steady-state approximation to the radical species ($PhCH_2\cdot$ and BNA·) involved in the initiation (eq 6–8), the propagation (eqs 18 and 19), and the termination (eq 21) steps, the rate of the disappearance of BNAH r is expressed by eq 22,

$$r = -\frac{d[BNAH]}{dt} = k_p(R_i/2k_t)^{1/2}[BNAH] \tag{22}$$

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(29) The cyclic voltammetry of benzyl bromide in MeCN containing Et_4NBr was reported to exhibit a single irreversible cathodic peak ($E^p = -1.11$ V vs. a AgBr|Ag reference at 100 mV s^{-1}); ref 18.

(30) The rate of the electron-transfer reaction of BNAH* with 1.34×10^{-3} M electron acceptors is evaluated as 2.1×10^{-9} M s^{-1} by using the diffusion rate constant (2.0×10^{10} M^{-1} s^{-1}), while the rate with 7.60×10^{-1} M benzyl bromide is 7.9×10^{-8} M s^{-1}.

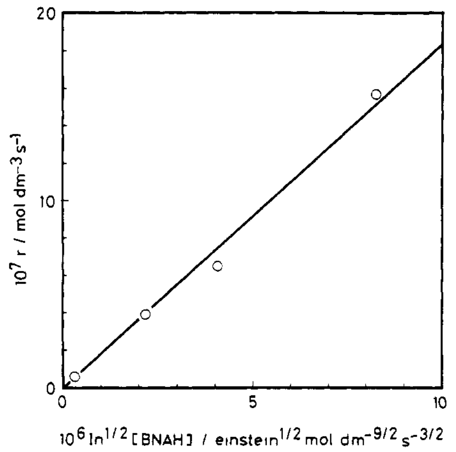

Figure 4. A plot of the rate of the photochemical reaction of BNAH with benzyl bromide in MeCN containing 1.11 × 10^{-1} M pyridine (r) as a function of $In^{1/2}$[BNAH]; see eq 12 and 22 in text.

where R_i is the initiation rate given by eq 12. From eqs 22 and 12 is derived eq 23,

$$\frac{1}{r^2} = C\left(\frac{1}{k_q\tau[\mathrm{PhCH_2Br}]}+1\right) \qquad (23)$$

where C is given as $2k_t[\mathrm{BNAH}]^{-2}/(k_p{}^2\Phi_f{}^0 In)$. The validity of eq 23 is confirmed by the plots of $1/r^2$ against $1/[\mathrm{PhCH_2Br}]$ which give a linear correlation under the conditions that the C value is constant (i.e., a fixed concentration of benzyl bromide and a constant light intensity), as shown in Figure 3a. The relation of eq 23 is applicable also for *p*-cyanobenzyl bromide by taking its concentration for [$\mathrm{PhCH_2Br}$] as shown in Figure 3b. From the slope and the intercept in Figure 3, parts a or b, the k_q values for the electron-transfer reactions from BNAH* to benzyl bromide and *p*-cyanobenzyl bromide (eq 7) have been determined as 4.2 × 10^9 and 1.4 × 10^{10} $\mathrm{M^{-1}\ s^{-1}}$, respectively, which show excellent agreements with those determined independently from the fluorescence quenching of BNAH (4.9 × 10^9 and 1.3 × 10^{10} $\mathrm{M^{-1}\ s^{-1}}$, respectively, see Table III). Such agreements clearly demonstrate that the electron transfer from the excited-state BNAH* to benzyl bromide or *p*-cyanobenzyl bromide (eq 7) is solely responsible for the photoinitiation of the chain reaction.

The validity of the rate formulation (eq 22) is further confirmed by the dependence of the reaction rate on the BNAH concentration as well as the light intensity absorbed by BNAH in the presence of a fixed amount of benzyl bromide in solution, as seen in Figure 4 which shows a linear relation between r and $In^{1/2}$[BNAH]. By substituting the reported value of k_t for the benzyl radical (1.8 × 10^9 $\mathrm{M^{-1}\ s^{-1}}$)[31] into eq 22, the propagation rate constant k_p of hydrogen transfer from BNAH to benzyl radical (eq 18) can be evaluated as 1.6 × 10^4 $\mathrm{M^{-1}\ s^{-1}}$, which is the same order of magnitude as the rate constant of hydrogen transfer from BNAH to the hex-5-enyl radical (6.0 × 10^4 $\mathrm{M^{-1}\ s^{-1}}$).[5c]

Registry No. BNAH, 952-92-1; benzyl bromide, 100-39-0; *p*-cyanobenzyl bromide, 17201-43-3; methyl iodide, 74-88-4; isopentyl nitrite, 110-46-3; *p*-dinitrobenzene, 100-25-4.

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Optically Active Phosphines. Facile Preparation of the Optically Active *n*-Propylmethylbenzyl- and Methylphenylbenzylphosphine Oxides as Precursors to the Corresponding Tertiary Phosphines

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Abstract: The optically active phosphine oxides $\mathrm{MePhP(O)CH_2Ph}$ (**6**) and *n*-$\mathrm{PrMeP(O)CH_2Ph}$ (**9**) are readily prepared by a new route from the easily available, essentially optically pure, *O*-isopropyl *S*-alkyl methylphosphonothioates **4** and **7**. Two successive Grignard reactions give **6** in 52–55% and **9** in 18–24% overall chemical yields. Reductions of **6** and **9** with $\mathrm{PhSiH_3}$ afford the corresponding optically active phosphines $\mathrm{MePhCH_2Ph}$ (**1**) and *n*-$\mathrm{PrMePCH_2Ph}$ (**2**) of optical purities (45–70% and 53–57%, respectively) which are quite suitable for studies of the stereochemistries of reactions occurring at phosphorus. The relative ease of the procedure and the fact that both enantiomers are equally readily available especially recommend this route for the preparation of **1**. Moreover, no other experimentally detailed, published method for the preparation of an optically active trialkylphosphine such as **2** in reasonably high optical purity is available. The route to phosphine **1** depends on the use of a potentially tridentate ligand ($\mathrm{SCH_2CH_2OCH_2CH_2OCH_2CH_3}$) on phosphorus which activates **4** toward reaction with PhMgBr and also allows $\mathrm{CH_3CH_2OCH_2CH_2OCH_2CH_2}$ to be selectively displaced. Quite surprisingly, this displacement occurs with inversion of configuration at phosphorus by contrast to the retentive stereochemistry normally observed on reaction of *O*-alkyl *S*-alkyl methylphosphonothioates with Grignards. Evidence is also presented for the potential generality of this method for the preparation of optically active dialkylphenyl- and trialkylphosphines.

Optically active tertiary phosphines continue to be of interest for the study of the stereochemistries of reactions taking place at phosphorus and also as potential ligands in asymmetric catalysis.[1] The earliest practical preparations of optically active phosphines involved electrolysis of optically active phosphonium salts.[2] This approach was largely replaced by use of diastereomerically pure cholesteryl[3] and menthyl alkylarylphosphinates[4–6]

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