sample was degassed at room temperature ($\leq 10^{-5}$ torr) for 2 h; oxygen-free nitrogen was then added, and the tube was sealed. The rotated tube was irradiated at 12 ± 2 °C with the 450-W lamp ($NiSO_4$, K_2CrO_4 filters) for ≥20 h. Product extraction and analysis were as previously described.

Solution Photolysis. For direct irradiation experiments solutions of AIBN in benzene were deaerated by purging with nitrogen for 20 min and were then irradiated at 20 °C (air cooling) with the 450-W lamp (7-60 filter). Samples of AIBN plus benzophenone (0.0314 and 0.124 M, respectively) were degassed ($\leq 10^{-5}$ torr) by four freeze–thaw cycles at 77 K and were then sealed. The samples were irradiated with the 450-W lamp ($NiSO_4$, K_2CrO_4 filters) at 12 ± 2 °C. Products were analyzed by NMR as outlined above.

Ketenimine Hydrolysis. (1) UV Experiments. A slurry of dimethyl-*N*-(2-cyano-2-propyl)ketenimine was prepared by adding silica gel to a 1-mm cuvette containing a 0.113 M benzene solution of ketenimine. The mixture was stirred as much as possible to provide an even distribution of the adsorbate. The ketenimine decomposition was monitored by the decrease in its absorption band at 290 nm (Figure 1).

A 0.158 M AIBN solution (benzene) in a 1-mm cuvette was irradiated to ~50% conversion. The absorption due to ketenimine **3** decreased upon addition of silica gel to the cuvette. After 80 min the absorption at the 290-nm had decreased to $\sim^1/_4$ of its original intensity.

Photolysis of AIBN in a silica gel–benzene slurry showed a gradual decrease in the absorption at 360 nm (AIBN) but only a small increase at 290 nm, even after extensive irradiation. The spectrum of the sample was unchanged after 12 h in the dark.

(2) Preparative Experiments. Silica gel (2.8 g) was added to 5 mL of 0.113 M benzene solution of **3**. The mixture was stirred thoroughly and then left at 25 °C in the dark for 12 h. The sample was extracted and analyzed as described previously and was shown to consist of amide **6** (45%) and unreacted **3** (55%). Similar experiments always resulted in substantial amounts of ketenimine hydrolysis. The amide was isolated from one experiment and its identity confirmed by comparison with an authentic sample.

Measurement of Geminate Recombination. Samples of an equimolar mixture of AIBN-d_0 and ABIN-d_{12} in benzene, in silica gel–benzene slurries, and on dry silica gel were prepared, degassed, and irradiated (to ≥50% conversion) as outlined in the preceding sections. Amide **6** was isolated from the reaction mixtures by chromatography on silica gel plates, with 10% methanol/benzene being used as the eluent. The deuterium content in the amide was determined by mass spectral analysis of the molecular ion region (m/e 154 (d_0), 160 (d_6) and 166 (d_{12})). The intensities at m/e 154 and 160, I_{154} and I_{160}, respectively, were corrected for the secondary isotope on the mass spectral fragmentation by using eq 2 and 3, where I' refers to the corrected intensity. A standard

$$I'_{154} = (k_H/k_D)_T^{1/12} \quad (2)$$

$$I'_{160} = [(k_H/k_D)_T^{1/12}]^6 \quad (3)$$

amide sample consisting of equimolar **6**-d_0 and **6**-d_{12} was run directly before each sample so that changes in the isotope effect due to instrumental variations did not affect the results. The corrected data were then used to calculate β from eq 1.

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Registry No. 1, 78-67-1; **2**, 3333-52-6; **3**, 10551-67-4; **6**, 84213-57-0; 2-cyano-2-propyl radical, 3225-31-8.

Redox-Photosensitized Reactions. 11.[1] $Ru(bpy)_3^{2+}$-Photosensitized Reactions of 1-Benzyl-1,4-dihydronicotinamide with Aryl-Substituted Enones, Derivatives of Methyl Cinnamate, and Substituted Cinnamonitriles: Electron-Transfer Mechanism and Structure–Reactivity Relationships

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Reactions of 1-benzyl-1,4-dihydronicotinamide (BNAH) with aryl-substituted enones and derivatives of methyl cinnamate and cinnamonitrile (**1a–u**) are photosensitized by $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine). The reduction of carbon–carbon double bonds commonly requires the substitution of either an electron-withdrawing aryl group or two phenyl groups at the β-carbon atom of **1**. With enones which possess one aryl substituent with no extra electron-withdrawing group at the β position, the photosensitized reactions result in no two-electron reductions but give 1:1 adducts (**4d–h**) along with half-reduced dimers of olefins (**3d** and **3g**) and a half-oxidized dimer of BNAH (**5**). The observed results can be easily interpreted by assuming the intervention of 1-benzyl-3-carbamoyl-1,4-dihydropyridin-4-yl radical (BNA·) and half-reduced species (·**1**-H) as key intermediates that are formed by mediated electron–proton transfer from BNAH to **1** in which $Ru(bpy)_3^{2+}$ acts as a one-electron shuttle upon photoexcitation in the initial electron transfer. Whether BNA· undergoes electron transfer to or a radical-coupling reaction with ·**1**-H depends on steric and electronic properties of ·**1**-H which should be affected by the substituents at the radical center. Mechanistic implications for thermal reactions of NADH models with olefins in the dark are briefly discussed on the basis of these observations.

The reduction of carbon–carbon double bonds by 1,4-dihydropyridines (eq 1) is of biological interest as a model for enzymatic reductions of steroidal enones[2] and unsaturated fatty acids[3] involving the pyridine nucleotide co-

$$\underset{\mathbf{1}}{R^1R^2C{=}CR^3X} + NADH + H^+ \rightarrow \underset{\mathbf{2}}{R^1R^2CHCHR^3X} + NAD^+ \quad (1)$$

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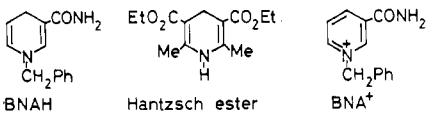
0022-3263/84/1949-0026$01.50/0

Table I. $Ru(bpy)_3^{2+}$-Photosensitized Reduction of 1a-c to 2a-c by BNAH[a]

entry[e]	R^1	R^2	R^3	$-E_{1/2}$[b]	convn of 1,[c] %	yields of 2,[c,d] %
a	p-C_6H_4CN	H	C_6H_5	1.76	95 (55)	89 (40)
b	p-$C_6H_4CO_2Me$	H	C_6H_5	1.82	95 (80)	90 (50)
c	C_6H_5	C_6H_5	H	2.00	40 (55)	25 (30)

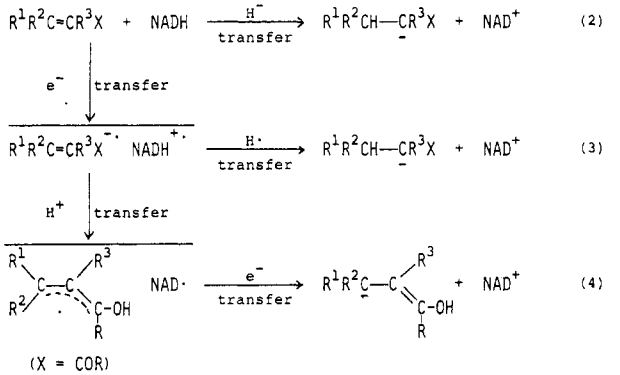
[a] For 3-mL solutions containing 1a-c (50 mM), BNAH (0.1 M), and $Ru(bpy)_3^{2+}$ (1 mM) irradiated at >470 nm for 1 h. [b] Polarographic half-wave reduction potentials in volts vs. $Ag/AgNO_3$ in MeCN by using a dropping mercury electrode and Et_4NClO_4 (0.1 M) as a supporting electrolyte. [c] Determined by GLC for 10:1 pyridine–methanol solutions. In parentheses are values for methanolic solutions. [d] Based on the 1a-c used. [e] X = COMe in all cases.

enzymes. However, nonenzymatic reductions by usual NADH models mostly require relatively high temperatures or activated substrates. Diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate, the Hantzsch ester, can



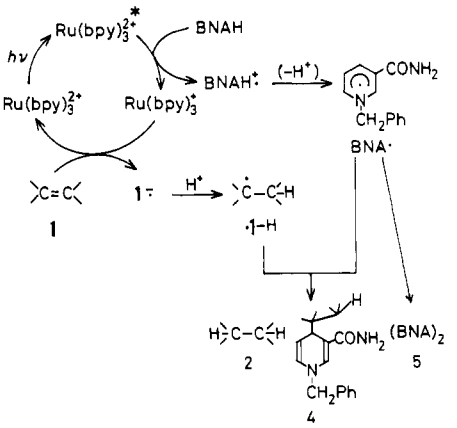
reduce maleic and fumaric acids, their esters, and related electron-deficient olefins only at >100 °C.[4] The reduction of 1-phenyl-4,4,4-trifluoro-2-buten-1-one can be achieved by the Hantzsch ester but not at all by 1-benzyl-1,4-dihydronicotinamide (BNAH), a more suitable model. More activated olefins such as benzylidenemalonate, α-cyanocinnamate, and benzylidenemalononitrile are reduced by BNAH or related models,[6-8] though the facile reduction requires the presence of acetic acid or magnesium ion. Zinc or magnesium ion is again essential for the reduction of 2-cinnamoylpyridine by BNAH or the Hantzsch ester.[9]

Although mechanisms are still unknown, it has been proved that hydrogen is transferred directly from the C-4 position of NADH models to the carbon atom β to the electron-deficient group (X).[5,6,9] Therefore, an ECE mechanism involving sequential electron–proton–electron transfer (eq 4) is pointed out to be unfavorable for the



reduction of enones.[9] A suggested mechanism involves direct hydride transfer (eq 2)[5,6,9] or electron transfer followed by hydrogen atom transfer (eq 3).[9] However, general applicability of the suggested mechanisms has not been demonstrated yet because of the restrictions of the available reaction systems. Therefore, either direct hydride transfer[5,6,9] or a stepwise mechanism involving electron transfer[8,9] may be true only for pertinent specific reaction systems; mechanistic pathways would depend on the substituents. the establishment of structure–reactivity relationships is thus requisite for the understanding of general mechanistic profiles.

Scheme I



In a previous paper,[10] we reported that $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) can photosensitize the facile reduction of dimethyl fumarate, dimethyl maleate, and some other olefins by BNAH, which proceeds via sequential two-electron transfer from BNAH to the olefins (Scheme I), an ECE mechanism corresponding to eq 4. The photosensitization can thus provide a mechanistic probe for electron-transfer reactions of NADH models as well as a clue to the establishment of structure-reactivity relationships in the reduction of olefins by way of ECE processes. The present paper deals with a systematic study on the $Ru(bpy)_3^{2+}$-photosensitized reactions of BNAH with aryl-substituted α,β-unsaturated ketones, carboxylates, and carbonitriles.

Results

Reduction of Enones. All the photosensitized reactions were carried out by visible-light irradiation of methanolic or 10:1 pyridine–methanol solutions containing an olefin (50 mM), BNAH (0.1 M), and $Ru(bpy)_3^{2+}$ (1 mM) at ≤20 °C. It was confirmed that no reaction occurs in the dark in any case. The progress of the reactions was followed by VPC or NMR and, in some cases, by HPLC. The enones used can be classified into two groups, one capable of being reduced to 2 and another undergoing no two-electron reduction but undergoing other reactions. Table

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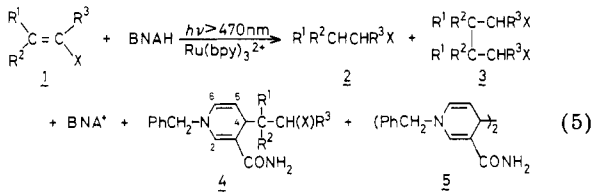
Table II. $Ru(bpy)_3^{2+}$-Photosensitized Reactions of BNAH with 1d-h[a]

entry[d]	R^1	R^3	X	$-E_{1/2}$, V	yields, % 3[b]	4[b]	5[c]
d	C_6H_5	H	COPh	1.78	4 (5)	15 (16)	13 (3)
e	p-C_6H_4Cl	H	COMe	1.92		13 (10)	13 (tr)
f	C_6H_5	H	COMe	2.02		37 (38)	15 (9)
g	C_6H_5	C_6H_5	COMe	2.04	2 (2)	4 (9)	12 (7)
h	p-C_6H_4OMe	H	COMe	2.12		10 (18)	18 (4)

[a] For 100-mL solutions containing 1d-h (50 mM), BNAH (0.1 M), and $Ru(bpy)_3^{2+}$ (1 mM) irradiated at >470 nm until 1d-h had been completely consumed. [b] Isolated yields based on the 1d-h used for 10:1 pyridine-methanol solutions and for methanolic solutions (in parentheses). [c] Based on the BNAH used. [d] R^2 = H in all cases.

I shows the results of the photosensitized reactions of the former group (1a–c). The reduction of 1a and 1b was efficient and favored the 10:1 pyridine–methanol solvent more than methanol. On the other hand, no significant solvent effect was observed in the reduction of 1c which was slow and not completed even on irradiation for much longer time.

In cases of 1d–h, the photosensitized reactions did not give 2 but complex mixtures, from which 3d,g, 4d–h, and 5 (eq 5) could be isolated; such reduced dimers as 3d and



(5)

3g could not be obtained in the other cases. Column chromatography on basic alumina was found to be convenient for isolation of compounds 4 and 5 except for 4f; rapid elution gave several fractions of mixtures from which 4 or 5 was crystallized out upon adding cold methanol. On the other hand, 4f was directly obtained by adding cold methanol to condensed photolysates. Each product isolated is one of the possible diastereomers. Compounds that were supposed to be the diastereoisomers of 4d–h were detected by NMR spectra of mixtures containing 4d–h. However, repeated column chromatography, TLC, and HPLC of the mixtures caused only substantial losses of materials without separation of any definite compound. Table II shows isolated yields of 3d, 3g, 4d–h, and 5. Low yields of the products are perhaps due to the failure in isolation of possible diastereoisomers as well as to partial decomposition of 4d–h during the chromatographic separation.

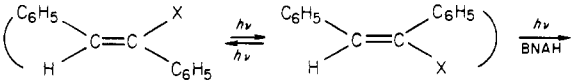
The assigned structures of the isolated products are in accord with the spectroscopic properties. Table III shows major fragment peaks in the mass spectra of 3d and 3g which demonstrate the β,β' dimer structures. Moreover, the ^1H NMR spectrum of 3g exhibits resonances at δ 3.96–4.30 as multiplets for unequivalent methine protons but none for methylene protons. The common 4-substituted 1,4-dihydronicotinamide structures of 4d–h are easily assignable from similar spectroscopic features involving strong UV absorption maxima at 338–345 nm, the basic fragment peak at m/e 213 in the mass spectra, and characteristic ^1H NMR signals for the C-2, C-4, C-5, and C-6 protons of the dihydropyridine ring; Table IV summarizes the major spectroscopic properties of 4d–h.

Reduction of Substituted Cinnamates and Cinnamonitriles. Table V shows the results of photosensitized reactions with 1i–s. No attempt was made for isolation and identification of other products. In cases of 1l and 1r, the reactions were slow and not completed even by irradiation for much longer time. The photoreduction of

Table III. Mass Spectral Data of 3d and 3g

compd	MS, m/e	assignment (rel intens)
3d	418	M^+ (10)
	299	$C_6H_5CHCH(C_6H_5)CH_2COPh^+$ (41)
	298	$C_6H_5CHC(C_6H_5)CH_2COPh^+$ (26)
	209	$(M/2)^+$ (100)
3g	446	M^+ (4)
	313	$C_6H_5CHCH(C_6H_5)CH(C_6H_5)COMe^+$ (53)
	269	$C_6H_5CHC(C_6H_5)CHC_6H_5^+$ (21)
	223	$(M/2)^+$ (13)
	180	$C_6H_5CHCHC_6H_5^+$ (100)
	134	$C_6H_5CHC(OH)Me^+$ (24)
	133	$C_6H_5CHCOMe^+$ (14)

1q was accompanied by E,Z isomerization, while the geometric isomerization was exclusive in case of 1k (eq 6).



1k, X = CO_2Me
q, X = CN

$C_6H_5CH_2CH(C_6H_5)CN$ (6)
2q

Discussion

Photochemical Electron-Transfer Process. The incident light at >470 nm can excite only $Ru(bpy)_3^{2+}$; no photoreaction took place in the absence of the ruthenium complex. The luminescence of $Ru(bpy)_3^{2+}$ was quenched by BNAH while the olefins are poor quenchers with a few exceptions (Table VI). It is probable that the efficient luminescence quenching by 1k and 1q arises from triplet energy transfer from excited $Ru(bpy)_3^{2+}$ to the olefins possessing the stilbene chromophore, which results in the E,Z isomerization.[11] On the other hand, it is now well-known that quenching of the $Ru(bpy)_3^{2+}$ luminescence generally involves electron transfer.[12-14] The observed rate constant for the luminescence quenching by BNAH in acetonitrile falls on a value predicted for electron transfer from an electron donor to $Ru(bpy)_3^{2+}$ in the luminescent excited state according to the Rehm–Weller's treatment[15] using eq 7–10,[13] where A = $Ru(bpy)_3^{2+}$, D =BNAH, E-

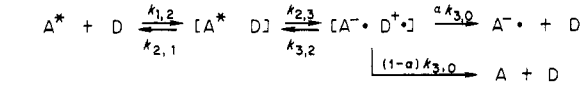


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Table IV. Spectroscopic Properties of 4d-h

compd	chemical shifts in ^{1}H NMR spectra[a] (J, Hz)								λ_{max},[b] nm (ϵ, M^{-1} cm^{-1})	MS, m/e[c] (M^+)
	H-2[d]	H-4	H-5	H-6	NCH_2	$CONH_2$	COMe	R^1R^2C[d]	$R^3CH(X)$	others		
4d	6.50	3.16-3.84	4.66 (5, 8)	5.60 (2, 8)	3.09	6.37		3.16-3.84	3.16-3.84	6.95-8.03	344 (4800)	422
4e	6.64	3.68 (3, 5)	6.68 (5, 8)	5.68 (2, 8)	4.00	6.38	2.16	3.38	2.56 (3, 18)	6.91-7.40	338 (5300)	393
4f	6.60	3.70 (3, 5)	4.68 (5, 8)	5.65 (2, 8)	4.00	6.25	2.21	3.42	2.66 (3, 18), 3.18 (11, 18)	6.92-7.40	345 (5000)	360
4g	6.58	3.88[d]	4.81 (5, 8)	5.72 (2, 8)	3.93	6.38	2.19	3.86	4.38 (12)	6.92-7.40	339 (4500)	436
4h[e]	6.64	3.67 (3, 5)	4.67 (5, 8)	5.66 (2, 8)	4.03	6.32	2.18	3.38	2.60 (3, 18), 3.10 (11, 18)	6.70-7.40	338 (6500)	390

[a] For $CDCl_3$ solutions in parts per million from Me_4Si. [b] Absorption maxima in CH_3CN. [c] A basic peak commonly appears at m/e 213. [d] Multiplet. [e] A sharp singlet for OCH_3 appears at δ 3.80.

$$k_q^{calcd} = \frac{k_{1,2}}{1 + \frac{k_{1,2}}{\Delta V k_{3,0}}\left[\exp\left(\frac{\Delta G_{2,3}^{\ddagger}}{RT}\right) + \exp\left(\frac{\Delta G_{2,3}}{RT}\right)\right]} \quad (8)$$

$$\Delta G_{2,3}^{\ddagger} = G_{2,3}/2 + [(\Delta G_{2,3}/2)^2 + (\Delta G^{\ddagger}(0))^2]^{1/2} \quad (9)$$

$$\Delta G_{23} = -E(A^*/A^{-}\cdot) + E(D/D^{+}\cdot) \quad (10)$$

$(D/D^{+}\cdot) = 0.76$ V vs. SCE in acetonitrile,[16] $E(A^*/A^{-}\cdot) = 0.7$ V vs. SCE in acetonitrile,[13,17] $\Delta G^{\ddagger}(0) = 4$ kcal/mol,[13] $\Delta V k_{3,0} = 8 \times 10^{11}$ M^{-1} s^{-1},[13] $k_{12} = 10^{10}$ M^{-1} s^{-1}, and $T = 293$ K. The calculated value (k_q^{calcd}) is 2.4×10^8 M^{-1} s^{-1}, very close to the observed rate constant. Therefore, it is strongly suggested that electron transfer is the primary process responsible for the photosensitized reactions. The quantum yields (α) for the net electron transfer giving the reactive redox intermediates appear to be greater than 0.44 in methanol and 0.55 in 10:1 pyridine–methanol as the solvent, the highest observed quantum yields for the disappearance of the olefins in the respective solvents (vide infra).

Alternatively, $Ru(bpy)_3^{2+}$ in a nonluminescent excited state would abstract a hydrogen atom from a solvent molecule to generate $Ru(bpy)_3H^{2+}$, a mechanism suggested by Kellog et al.[18] for the $Ru(bpy)_3^{2+}$-photosensitized reduction of activated sulfonium salts by NADH models of structures similar to the Hantzsch ester. The mechanistic argument is based on the observation that no apparent quenching of the $Ru(bpy)_3^{2+}$ luminescence occurred at $\leq 10^{-3}$ M in the NADH model. Recently the population of a nonluminescent d–d state by crossing from the charge-transfer luminescent state has been demonstrated to become significant in the absence of quenching of the latter state and especially at higher temperatures.[19] A major chemical consequence from the d–d state is, however, ligand substitution (eq 11).[19,20]

$$Ru(bpy)_3^{2+*}_{^3CT} \rightarrow Ru(bpy)_3^{2+*}_{^3d\text{-}d} \xrightarrow{2L} Ru(bpy)_2L_2^{2+} + bpy \quad (11)$$

In the present photoreactions, however, the involvement of a nonluminescent state is very unlikely since the reactions were conducted at 0.1 M in BNAH where the luminescence of $Ru(bpy)_3^{2+}$ was completely quenched. In fact, neither the consumption of $Ru(bpy)_3^{2+}$ nor the formation of free bpy was observed in any case even after the photosensitized reactions had reached the maximum conversions. Generally speaking, mechanistic arguments based on luminescence quenching by inefficient quenchers at low concentrations should be examined with care since pertinent photosensitized reactions usually employ high concentrations of quenchers. Complete or dominant quenching of the $Ru(bpy)_3^{2+}$ luminescence can be easily achieved even by inefficient quenchers since lifetimes of the luminescent state are very long. Moreover, low values of k_q are not necessarily associated with net low yields of electron transfer but indicate only the endergonic nature

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Table V. $Ru(bpy)_3^{2+}$-Photosensitized Reduction of 1i-s to 2i-s by BNAH[a]

entry	R^1	R^2	R^3	X	$-E_{1/2}$, V	time,[b] h	convn of 1,[c] %	yields of 2,[c,d] %
i	p-C_6H_4CN	H	H	CO_2Me	1.80	0.8	100 (70)	100 (40)
j	p-$C_6H_4CO_2Me$	H	H	CO_2Me	1.87	1.0	75 (50)	60 (25)
k	C_6H_5	H	C_6H_5	CO_2Me	2.14	1.0	[e]	
l	C_6H_5	C_6H_5	H	CO_2Me	2.18	2.0	17 (23)	9 (20)
m	C_6H_5	H	H	CO_2Me			no reaction	
n	p-C_6H_5CN	H	H	CN		[f]	~80 (~50)	~60 (~25)
o	H	p-C_6H_4CN	H	CN		[f]	~80 (~60)	~70 (~30)
p	p-$C_6H_4CO_2Me$	H	H	CN		1.0	58	33
q	H	C_6H_5	C_6H_5	CN	1.95	2.0	100 (100)	33[g] (13[h])
r	C_6H_5	C_6H_5	H	CN	2.14	4.0	22	10
s	C_6H_5	H	H	CN			no reaction	

[a] For 3-mL solutions containing 1i-s (50 M), BNAH (0.1 M), and $Ru(bpy)_3^{2+}$ (1 mM) irradiated at >470 nm. [b] Irradiation time. [c] Determined by GLC for 10:1 pyridine-methanol solutions and for methanolic solutions (in parentheses). [d] Based on the 1i-s used. [e] No reduction but exclusive E,Z isomerization. [f] For 100-mL solutions irradiated for 1.5 h. Both conversions and yields were determined by NMR. [g] The Z isomer was formed in 35% yield. [h] The Z isomer was formed in 85% yield.

Table VI. Rate Constants for Quenching of $Ru(bpy)_3^{2+}$ Luminescence[a]

quenchers	solvent	τ,[b] μs	$k_q\tau$, M^{-1}	k_q, M^{-1} s^{-1}
BNAH	MeOH	0.83	120	1.5×10^8
	MeCN	1.00	294	2.9×10^8
	DMF[c]	0.93	184	2.0×10^8
	py-MeOH[d]	1.03	358	3.5×10^8
5	py-MeOH		1700	1.7×10^9
DMT[e]	MeOH		820	9.9×10^8
1g	MeOH		9	1.1×10^7
1k	MeOH		920	1.1×10^9
1q	MeCN		210	2.1×10^8
other olefins	MeCN		<5	$<<10^7$

[a] Determined by Stern-Volmer plots of the luminescence quenching for deaerated solutions by 550-nm excitation. [b] Observed lifetimes of the $Ru(bpy)_3^{2+}$ luminescence. [c] N,N-Dimethylformamide. [d] 10:1 pyridine-methanol solvent. [e] N,N-Dimethyl-p-toluidine.

of the electron-transfer process. It was reported that net quantum yields of photochemical electron transfer are moderate (0.2–0.3) in cases of some ruthenium(II) complex–aliphatic amine pairs where k_q's are low ($\sim 10^8$ M^{-1} s^{-1}).[21]

Mechanistic Pathways and Reactive Species in Olefin Reduction. We previously reported that the $Ru(bpy)_3^{2+}$-photosensitized reduction of dimethyl fumarate and maleate in methanol-d resulted in dominant incorporation of two deuterium atoms in the reduced product (dimethyl succinate) while no deuterium incorporation was observed in the reactions with BNAH-*4,4-d_2*.[10] These observations unambiguously eliminate the involvement of either direct hydride or hydrogen atom transfer in the photosensitized reduction. Moreover, the participation of disproportionation of half-reduced species was proved to be negligible since neither deuterium incorporation in the recovered olefins nor stereomutation of the starting olefins occurred. The mechanism can be easily interpreted in terms of sequential two-electron transfer to the olefins (Scheme I and eq 12). It is therefore reasonable to presume that this mechanism can apply for the present photosensitized reactions.

$$MeO_2CCH{=}CHCO_2Me \xrightarrow[D^+]{e^- (Ru(bpy)_3^{+})} MeO_2C\text{-}C(D)H\text{-}\dot{C}H\text{-}CO_2Me \xrightarrow[D^+]{e^- (BNA\cdot)} MeO_2C\text{-}CH(D)CH(D)\text{-}CO_2Me \quad (12)$$

(21) Monserrat, K.; Foreman, T. K.; Grätzel, M.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 6667.

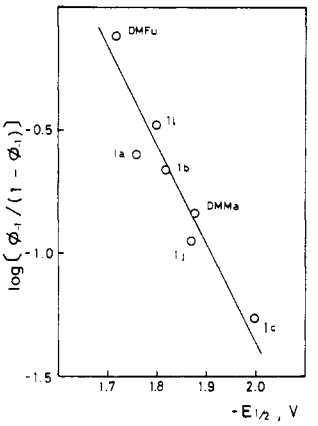
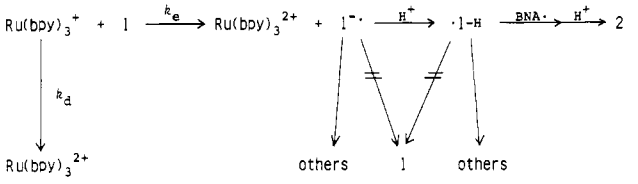


Figure 1. Plot of log $[\phi_{-1}/(1 - \phi_{-1})]$ vs. reduction potentials ($E_{1/2}$) for the photosensitized reactions of methanolic solutions. For the abbreviations of olefins see Tables I, II, and V, and DMFu and DMMa denote dimethyl fumarate and dimethyl maleate, respectively.

Scheme II



The reduction potential of $Ru(bpy)_3^{2+}$ (−1.69 V) is more positive than but similar to those of the olefins. The polarographic reduction waves of the olefins are probably due to reversible one-electron transfer since reversibility in one-electron reduction of enones has been proved by cyclic voltammetry.[22] The electrochemical data can therefore be used to estimate free-energy changes for electron transfer from $Ru(bpy)^+$ to the olefins which are positive by 1–10 kcal mol^{-1}. As predicted by the Marcus equation[23] or the related empirical modifications,[15,24] a linear free energy relationship may hold for such an endergonic process. Table VII lists quantum yields for the disappearance of 1 (ϕ_{-1}) as well as for the formation of 2 (ϕ_2) for some olefins together with the data for dimethyl

(22) Bowers, K. W.; Giese, R. W.; Grimshaw, J.; House, H. O.; Kolodny, N. H.; Kronberger, K.; Roe, D. K. *J. Am. Chem. Soc.* **1970**, *92*, 2783.

(23) Markus, R. A. *J. Chem. Phys.* **1956**, *24*, 966; *Discuss. Faraday Soc.* **1960**, *29*, 21.

(24) Scandola, F.; Balzani, V.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 2519.

Table VII. Quantum Yields for Disappearance of 1 and Formation of 2

entry	R^1	R^2	R^3	X	$-E_{1/2}$, V	ϕ_{-1} [a,b]	μ ϕ_2 [a,c]
	CO_2Me	H	H	CO_2Me	1.72	0.44 (0.44)	0.33 (0.029)
	H	CO_2Me	H	CO_2Me	1.88	0.20 (0.13)	0.20 (0.060)
a	p-C_6H_4CN	H	C_6H_5	COMe	1.76	0.26 (0.20)	0.25 (0.066)
b	p-$C_6H_4CO_2Me$	H	C_6H_5	COMe	1.82	0.28 (0.18)	0.28 (0.078)
c	C_6H_5	C_6H_5	H	COMe	2.00	0.053 (0.056)	0.030 (0.038)
i	p-C_6H_4CN	H	H	CO_2Me	1.80	0.55 (0.25)	0.55 (0.18)
j	p-$C_6H_4CO_2Me$	H	H	CO_2Me	1.87	0.37 (0.10)	0.31 (0.079)

[a] Determined by the irradiation at 520 nm for deaerated 10:1 pyridine–methanol solutions and for methanolic solutions (in parentheses) containing an olefin (50 mM), BNAH (0.1 M), and $Ru(bpy)_3^{2+}$ (2.7 mM). [b] Quantum yields for the disappearance of the starting olefins. [c] Quantum yields for the formation of 2.

fumarate and maleate. As is shown in Scheme II and eq 13, ϕ_{-1} can serve to show the dependence of k_e on $E_{1/2}$,

$$\phi_{-1}/(\alpha - \phi_{-1}) = k_e/k_d \quad (13)$$

provided that regeneration of 1 from $1^{-\cdot}$ and ·1-H is not important. Eventually log $[\phi_{-1}/(1 - \phi_{-1})]$ was plotted against $E_{1/2}$ since α is unknown. A linear correlation in Figure 1 demonstrates that the disappearance of 1 involves one-electron transfer in a rate-determining step.

A key species in the one-electron reduction of ·1-H is BNA· that is readily formed by the loss of a proton from the cation radical of BNAH ($BNAH^{+\cdot}$, eq 14). In the

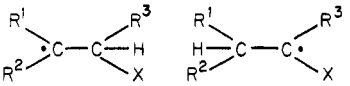
$$BNAH^{+\cdot} \xrightarrow[(-H^+)]{\text{pyridine or BNAH}} BNA\cdot \quad (14a)$$

$$BNAH^{+\cdot} \xrightarrow[(-H^+)]{} \text{others} \quad (14b)$$

absence of an added base, BNAH can act as a base to receive a proton from $BNAH^{+\cdot}$ in competition with other reactions.[25] In 10:1 pyridine–methanol solvent, however, the deprotonation process predominates over other pathways, thus giving BNA· in higher steady-state concentration. This is in line with the observations that ϕ_2's and yields of 5 remarkably increase upon changing solvent from methanol to 10:1 pyridine–methanol in most cases. Since electron transfer from BNA· to $Ru(bpy)_3^{2+}$ and neutral molecules of 1 appears to be very slow because of relatively high endothermicity of this process, BNA· might survive long enough to undergo follow-up processes. On the other hand, the participation of $Ru(bpy)_3^+$ in the reduction of ·1-H to 2 is not important since this species is probably scavenged by large excess of neutral molecules of 1.

With regard to the two-electron-reduction capabilities of BNAH, it should be noted that neither *N,N*-dimethyl-*p*-toluidine (DMT) nor 5 can be used as a two-electron reductant instead of BNAH, though the luminescence of $Ru(bpy)_3^{2+}$ is quenched by DMT and 5 at 9.9×10^8 and 1.7×10^9 M^{-1} s^{-1} in methanol, respectively. The $Ru(bpy)_3^{2+}$-photosensitized reactions of **1a** with DMT in methanol or 10:1 pyridine–methanol solvent resulted in no or little (<5%) reduction of **2a**, but each gave complex mixtures. In the case of dimethyl maleate, no reduction but dominant formation of complex mixtures again occurred in the photosensitized reactions with DMT in methanol as well as with 5 in *N,N*-dimethylformamide. Unique reactivities of BNAH capable of donating two electrons to a substrate molecule seem to originate from facile formation of BNA· after the first one-electron transfer as well as from the relatively low oxidation potential of this radical intermediate.

Structure–Reactivity Relationships in Two-Electron Reduction and Adduct Formation. The two-electron reduction can occur in cases where R^1 = p-C_6H_4CN or p-$C_6H_4CO_2Me$ and R^2 = H or $R^1 = R^2 = C_6H_5$ irrespective of X. On the other hand, the enones that contain neither such an extra electron-withdrawing group nor the two phenyl groups at the position β to X are not reduced to **2** but give **4**. These reactivity differences associated with R^1 and/or R^2 suggest that a prefered structure of ·1-H should be ·1-H(A) rather than ·1-H(B), a structure assignment supported by the structures of **3d,g** and **4d–h**.



·1-H(A) ·1-H(B)

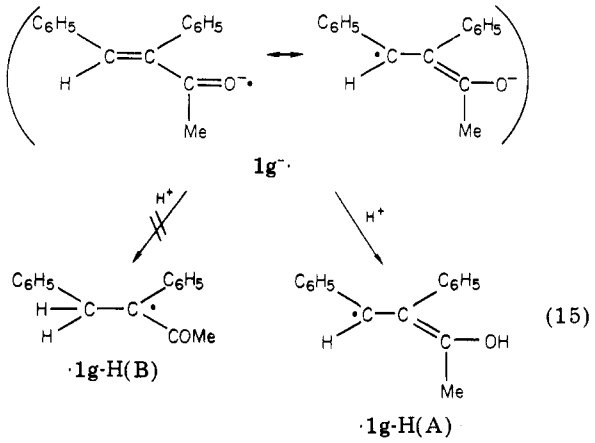
Reduction potentials of ·1-H(A) should depend on R^1 and R^2 but not on R^3 and X. In cases where R^1 = p-C_6H_4CN or p-$C_6H_4CO_2Me$ the strong electron-withdrawing nature of the substituents certainly enhances the electron-accepting power of the radicals. On the other hand, ·1-H(A), which contains no such extra electron-withdrawing group but only one aryl substituent at the beta position, does not have a reduction potential enough positive to be reduced by BNA·, thus undergoing dimerization and radical-coupling reactions to give 3 and 4. The substitution of the two phenyl groups at the β position appears to make the radicals capable of receiving an electron from BNA· to some extent, probably by combined inductive effects of the two phenyl groups as well as by an extended cross section for electron transfer due to greater delocalization of an odd electron; these effects appear not to be large since the ϕ_2 values are very small for the pertinent reaction systems. Moreover, steric hindrance of the two phenyl groups that prevents radical-coupling reactions should be taken into account as an additional effect allowing slow electron transfer from BNA· to ·1-H to ensue.

It should be stressed that the above discussion is valid only for ·1-H(A). In cases where R^1 and/or R^2 = aryl and R^3 = H, ·1-H(A) is certainly more stable than ·1-H(B) because of greater resonance stabilization by the aryl group(s). However, the reverse may happen when R^3 = C_6H_5; i.e., ·1-H(B) is more stable. The radical intermediates from **1g**, **1k**, and **1q** would fit the case. The one-electron reduction of ·1-H(B) by BNA· may occur since the strong electron-withdrawing group (X) directly attaches to the free-radical center.

In contradiction to the expectation, **1g** was not reduced to **2g**, and the structures of the isolated products (**3g** and **4g**) demonstrate that ·1-H(A) is formed as a reactive intermediate (eq 15). According to the reported ESR studies on the anion radicals of enones.[22,26] about half of the unpaired electron density is located at the β carbon atom and the other half at the carbonyl group with little or no spin density at the α carbon atom. Therefore, it is probable that the carbonyl oxygen of the anion radical of enones is selectively protonated to leave the spin density at the β

(25) Blaedel, W. J.; Haas, R. G. *Anal. Chem.* **1970**, *42*, 918.

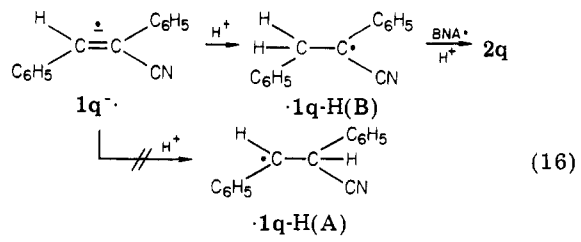
(26) Russel, G. A.; Stevenson, G. R. *J. Am. Chem. Soc.* **1971**, *93*, 2432.



(15)

carbon atom irrespective of R^3; no reduction of **1g** to **2g** can thus be expected since ·**1g**-H(A) is a benzylic radical with no extra electron-withdrawing substituent.

On the other hand, since the photosensitized reduction of **1q** to **2q** occurs (eq 16), it is suggested that the anion



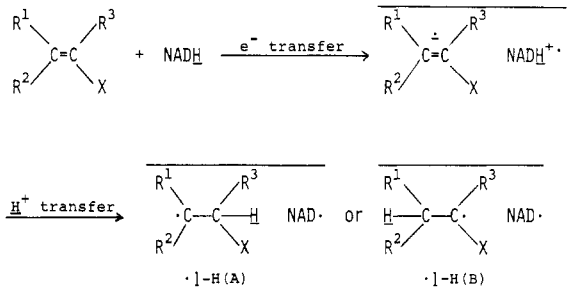
(16)

radical of **1q** ia protonated at the β carbon atom to yield a more stable radical ·**1q**-H(B). It is highly probable that this radical is capable of being reduced by BNA· because of a strong electron-withdrawing effect of the nitrile group. In contrast, protonation at the α carbon atom would afford less stable radical ·**1q**-H(A) which should be incapable of receiving an electron from BNA· as expected from the electronic structure very similar to those of ·**1g**-H(A) and related benzylic radicals with no strong electron-withdrawing substituent. In case of **1k** which is a carboxylate analogue of **1g** and **1q** (i.e., X = CO_2Me), unfortunately, nothing can be discussed with respect to the structures and reactivities of ·1-H since the *E,Z* isomerization exclusively occurs without redox reactions.

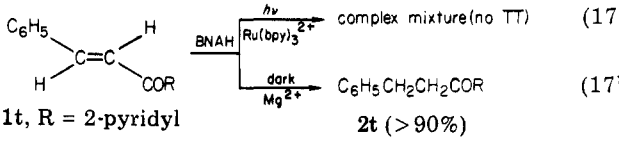
Mechanistic Implications for Thermal Reduction of Carbon–Carbon Double Bonds by NADH Models. The present results clearly demonstrate that BNAH and probably other similar NADH models are capable of donating two electrons to a molecule of olefin via ECE processes. Therefore, an ECE mechanism is a possible, but not obligatory, choice for thermal reduction of carbon–carbon double bonds by NADH models as suggested earlier.[10] Since reduction of some olefins in the dark involves direct hydrogen transfer to the carbon atom β to X,[5,6,9] however, this mechanism may hold only in cases where ·1-H(B) is formed (Scheme III). If so, it is evident that thermal reduction of enones does not fit the case since the intervention of ·1-H(A) appears to be an inevitable consequence of sequential electron-proton transfer to enones as discussed in the previous section.

In order to obtain further insights into mechanistic aspects of thermal reduction of enones, $Ru(bpy)_3^{2+}$-photosensitized reactions were compared with thermal reactions by using (*E*)-2-cinnamoylpyridine (**1t**) and (*Z*)-1-(2-pyridyl)-2-phenyl-1-buten-3-one (**1u**). Thermal reactions were conducted in the presence of Mg^{2+} in methanol at 20 °C since no reaction occurred in the absence of Mg^{2+} even upon heating. In case of **1t**, the Mg^{2+}-catalyzed reduction

Scheme III

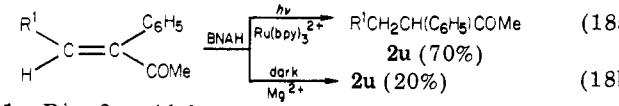


was very efficient as reported,[9] while the photosensitized reaction did not give **2t** at all but complex mixtures (eq 17). In contrast, the reduction of **1u** in the dark was



(17a)

(17b)



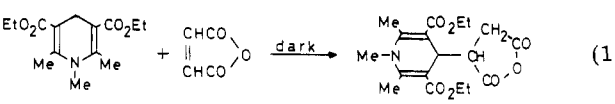
(18a)

(18b)

inefficient, unlike the efficient photosensitized reduction (eq 18).

The different behaviors of **1t** and **1u** in the photosensitized reactions are strictly in line with those of **1d–h** and **1a–c**, respectively, demonstrating again the intermediacy of ·1-H(A) in these photosensitized reactions. On the other hand, it is highly improbable that similar mechanisms involving ·1-H(A) are operative in both the photosensitized and thermal reactions of either **1t** or **1u**, since no correlation was observed between them. Especially, the facile reduction of **1t** by catalysis of Mg^{2+} in the dark disagrees with a simple ECE mechanism, unless specific interactions of Mg^{2+} with **1t**[9] would allow the intervention of ·1-H(B) as a consequence of electron-proton transfer.

On the other hand, thermal reduction of cyanated olefins may proceed via ECE processes in cases where ·1-H(B) is more stable than ·1-H(A); alkylidenemalononitriles which are reduced by NADH models[6] fit the case. Although mechanistic aspects of thermal reduction of unsaturated carboxylic acids and their derivatives remain unsolved, it is of interest to note that the dark reaction of maleic anhydride with an NADH model affords a 1:1 adduct of a structure very similar to those of **4** (eq 19),[27] a result im-



(19)

plying the involvement of electron–proton transfer from the model to the substrate. Unfortunately, no further discussion can be made since any other example of the adduct formation in the dark has not appeared.

Experimental Section

Materials. Methanol was distilled from magnesium methoxide. Pyridine was refluxed over anhydrous potassium hydroxide and then distilled before use. BNAH[28] and $Ru(bpy)_3Cl_2·6H_2O$[29] were

(27) Sims, A. F. E.; Smith, P. W. G. *Proc. Chem. Soc.* **1958**, 282.
(28) Mauzarall, D.; Westheimer, F. M. *J. Am. Chem. Soc.* **1955**, *77*, 2261.
(29) Fujita, I.; Kobayashi, H. *Ber. Busenges. Phys. Chem.* **1972**, *70*, 115.

prepared and purified according to the literature methods. Dimethyl fumarate, dimethyl maleate, and **1d,f,m,s** were reagent grade (Tokyo Kasei). The following known olefins were prepared according to published methods: **1c**, bp 200–205 °C (15 torr) [lit.[30] bp 103–105 °C (0.01 torr)]; **1e**, mp 56–57.5 °C (lit.[31] mp 59–59.5 °C); **1g**, mp 54–56 °C (lit.[32] mp 56 °C); **1k**, mp 73–74 °C (lit.[33] mp 76 °C); **1q**, mp 86–87 °C (lit.[34] mp 88 °C); **1r**, mp 48–49 °C (lit.[35] mp 49–50 °C); **1t**, mp 67–69 °C (lit.[36] mp 71–72 °C). Procedures employed for the preparation of **1g**[32] were adopted to obtain **1a** (mp 97–99 °C), **1b** (mp 103–105 °C), and **1u** (mp 32–33 °C); a benzene solution (35 mL) containing phenylacetone (23 mmol), an aromatic aldehyde (22 mmol), and piperidine (0.5 g) was refluxed for 12 h with the use of a Dean–Stark water separator and then distilled in vacuo to give solids, which were recrystallized from a mixture of hexane and benzene. *p*-Methoxybenzalacetone (**1h**, mp 66–67 °C) was prepared by a condensation reaction of *p*-methoxybenzaldehyde with acetone in the presence of sodium hydroxide according to the method employed for the preparation of **1e**.[31] Methyl *p*-cyanocinnamate (**1i**, mp 125–126 °C) was prepared by the esterification of the parent carboxylic acid which was obtained from *p*-cyanobenzaldehyde and malonic acid.[37] An identical method in which *p*-(methoxycarbonyl)benzaldehyde was used in place of *p*-cyanobenzaldehyde was employed for the preparation of **1j** (mp 119–121 °C). Methyl β-phenylcinnamate (**1l**, bp 195–198 °C) was obtained by the esterification of the corresponding acid chloride prepared from 1,1-diphenylethylene and oxalyl chloride.[38] The preparation of **1n**, **1o**, and **1p** was carried out as follows. A 2:1 toluene–pyridine solution (15 mL) of *p*-cyanobenzaldehyde or *p*-(methoxycarbonyl)benzaldehyde (50 mmol), cyanoacetic acid (60 mmol), and ammonium acetate (0.16 g) was refluxed for 8 h, and then volatile materials were evaporated to dryness in vacuo. Sublimation of the residue gave crystalline materials which were subjected to column chromatography on silica gel (70–230 mesh, Merck) to separate the olefins: **1n**, mp 183–185 °C; **1o**, mp 138.5–139 °C; **1p**, mp 144–145 °C.

Analytical Methods. Melting points were taken on a hot stage and are uncorrected. GLC was performed on a Shimadzu GC-3BF dual column instrument with flame-ionization detectors and a 2 m × 4 mm column packed with 2% OV-17 on Shimalite W. HPLC was carried out on a JAI LC-09 by using an LS-225 ODS column. ^{1}H NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer, IR spectra on a Hitachi 260-10 spectrometer, UV and visible absorption spectra on a Hitachi 220-A spectrometer, and mass spectra on a Hitachi RMU-6E.

Reduction potentials were measured for N_2-saturated dry acetonitrile solutions (1 mM) vs. an $Ag/AgNO_3$ reference electrode at 20 ± 0.1 °C by using a dropping mercury electrode and a Yanagimoto P-1000 potentiostat. Tetraethylammonium perchlorate (0.1 M) was used as the supporting electrolyte. Luminescence-quenching experiments were performed on a Hitachi MPF-4 spectrofluorometer equipped with a data processor (Type 612-0085), and solutions were deaerated by passing a gentle stream of Ar through solutions for 20 min. The ruthenium complex (0.25 mM) was excited at 550 nm, and intensities of the luminescence were monitored at 610 nm. The luminescence lifetimes were determined by the use of an N_2 laser with a pulse width of 1 ns.

Quantum yields were determined for thoroughly degassed solutions containing an olefin (50 mM), BNAH (0.1 M), and $Ru(bpy)_3^{2+}$ (2.7 mM) by using Reinecke's salt as an actinometer.[39] The incident light at 520 nm was isolated from a xenon lamp by using a Hitachi MPF-2A monochromator, and the intensity was determined to be 2.57×10^{17} photons/min. All the procedures were performed in a dark room with a safety lamp. Both the disappearance of **1** and the formation of **2** were analyzed by GLC and plotted against time. Quantum yields were calculated from the slopes of initial linear portion of the plots.

Photosensitized Reactions of 1a–c and 1i–u. The light source was a Matushita tungsten–halogen lamp (300 W) immersed in a quartz well, outside of which was placed a double-cylindrical Pyrex vessel with a 1-cm space filled with a filter solution. This filter solution which was made by dissolving potassium chromate (20 g/L), sodium nitrate (200 g/L), and sodium hydroxide (6.7 g/L) in distilled water can completely cut off the light below 470 nm and was able to be used throughout the present investigation without any change in absorbance. The light source and the filter solution were set in the center of a "mercury-go-round" apparatus immersed in a water bath with circulation of cold water.

Methanolic or 10:1 pyridine–methanol solutions containing an olefin (50 mM), BNAH (0.1 M), and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (1 mM) were bubbled with a gentle stream of Ar for 15 min and then irradiated. The irradiation was carried out for 3-mL solutions in Pyrex tubes (8 mm i.d.) by using the merry-go-round apparatus under cooling with water except for the reactions of **1n** and **1o**, and the progress of the reactions was followed by GLC. The reactions of **1n** and **1o** were carried out on a greater scale and analyzed by ^{1}H NMR, since almost identical retention times of **1n**, **1o**, and **2n** (**2o**) did not allow GLC analyses. A double-cylindrical Pyrex vessel filled with a reactant solution (100 mL) was placed just outside of the filter-solution vessel and the mixture then irradiated for 1.5 h. After removal of the solvent in vacuo, the residue was chromatographed on silica gel. Elution with 500 mL of diethyl ether gave a mixture of the starting olefin, **2n** (**2o**), and BNAH as shown by ^{1}H NMR. The results are summarized in Tables I and V.

General Procedure for Isolation of 4d–h and 5. The irradiation was carried out for 100-mL solutions as described above. The complete disappearance of **1d–h** required the irradiation for 3–5 h. After removal of the solvent from the photolysate, chloroform (20 mL) was added to the residue to make a homogeneous solution, which was then added to 5 g of basic alumina (70–230 mesh, Merck Art 1076). After gentle evaporation of the chloroform with a rotary evaporator under reduced pressure, the alumina-supported photolysate was added to the top of a column of basic alumina (50 g) and then eluted with mixtures of methanol and diethyl ether. Elution with 500 mL of 10% methanol in diethyl ether gave unreacted BNAH (10–70 mg), whereas mixtures containing **4d–h** were eluted with 20–50% methanol in diethyl ether. To the mixtures were added minimal volumes of methanol to make homogeneous solutions, which were combined and then stored in a refregerator. Pale yellow solids were precipitated and filtered to give **4d–h**. Further elution with methanol gave red-brown materials to which a minimal volume of methanol was added, and then the mixture was cooled on an ice bath. A pale yellow solid was precipitated and filtered to give **5**. The isolation of **4f** was performed without the use of column chromatography as follows. After removal of the solvent from the irradiated solution, methanol (10 mL) was added to the residue to make a homogenous solution, which was then cooled on an ice bath. A pale yellow solid was precipitated and filtered to give **4f**. The filtrate was subjected to column chromatography to isolate **5** as described above. The isolated yields are listed in Table II. The products were recrystallized from ethanol, and the spectroscopic properties of **4d–h** are summarized in Table IV.

For **4d**: mp 183–185 °C dec. Anal. ($C_{28}H_{26}N_2O_2$) C, H, N.

For **4e**: mp 173–175 °C dec. Anal. ($C_{23}H_{23}ClN_2O_2$) C, H, N, Cl.

For **4f**: mp 206–207 °C dec. Anal. ($C_{23}H_{24}N_2O_2$) C, H, N.

For **4g**: mp 216–220 °C dec. Anal. ($C_{29}H_{28}N_2O_2$) C, H, N.

For **4h**: mp 179–181 °C dec. Anal. ($C_{24}H_{26}N_2O_3$) C, H, N.

For **5**: mp 173–174 °C dec; ^{1}H NMR (CD_3SOCD_3)[40] δ. 3.20 (d, J = 5 Hz, 1 H), 4.32 (dd, J = 5, 8 Hz, 1 H), 4.33 (s, 2 H), 5.95

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(dd, J = 2, 8 Hz, 1 H), 6.85 (br s, 2 H), 7.15 (m, 1 H), 7.23 (m, 5 H); mass spectrum, m/e 213 ($M^+/2$); UV (MeOH) λ_{max} 356 nm (ϵ 6900). Anal. ($C_{26}H_{26}N_4O_2$) C, H, N.

Isolation of 3d. The irradiation of a 100-mL methanolic or 10:1 pyridine–methanol solution for 3 or 4 h resulted in the complete disappearance of **1d**. In case of the 10:1 pyridine–methanol solution, the solvent was mostly evaporated in vacuo, and then methanol (10 mL) was added. White solids were precipitated upon cooling and then filtered to give **3d** (42 mg). The irradiated methanolic solution was condensed in vacuo to one-tenth of its volume to give **3d** (52 mg). This compound was recrystallized from a mixture of methanol and benzene: mp 273–276 °C; ^{1}H NMR ($CDCl_3$) δ 2.82–3.83 (m, 3 H), 7.02–7.80 (m, 10 H); IR (KBr) 1670 cm^{-1}. Anal. ($C_{30}H_{26}O_2$) C, H.

Isolation of 3g. After evaporation of the 100-mL methanolic or 10:1 pyridine–methanol solution (irradiated for 5 h) chloroform (30 mL) was added, and then the mixture was washed with diluted hydrochloric acid, saturated sodium bicarbonate, and brine. Evaporation of chloroform left a small amount of brownish oil, to which methanol (3 mL) was added, and then the mixture was cooled on an ice bath to give **3g** (5 mg) as a white solid: mp 254–255 °C (from methanol–benzene); ^{1}H NMR ($CDCl_3$) δ 1.78 (s, 3 H), 3.96–4.30 (m, 4 H), 6.70–7.20 (m, 10 H); IR (KBr) 1700 cm^{-1}. Anal. ($C_{32}H_{30}O_2$) C, H.

Registry No. **1a**, 87870-43-7; **1b**, 87870-44-8; **1c**, 837-66-1; **1d**, 614-47-1; **1e**, 30626-03-0; **1f**, 1896-62-4; **1g**, 38661-88-0; **1h**, 3815-30-3; **1i**, 67472-79-1; **1j**, 52148-89-7; **1k**, 36854-27-0; **1l**, 3461-34-5; **1m**, 1754-62-7; **1n**, 27519-25-1; **1o**, 79430-98-1; **1p**, 79430-99-2; **1q**, 6114-57-4; **1r**, 3531-24-6; **1s**, 1885-38-7; **1t**, 53940-12-8; **1u**, 87883-10-1; **2a**, 54636-71-4; **2b**, 54636-00-9; **2c**, 5409-60-9; **2i**, 75567-85-0; **2j**, 40912-11-6; **2** (R^1 = CO_2Me; R^2 = H; R^3 = H; X = CO_2Me), 106-65-0; **3d**, 7028-45-7; **3g**, 87870-45-9; **4d**, 87883-11-2; **4e**, 87870-46-0; **4f**, 87870-47-1; **4g**, 87870-48-2; **4h**, 87870-49-3; **5**, 67146-57-0; BNAH, 952-92-1; $Ru(bpy)_3^{2+}$, 15158-62-0.

Gossypium Cadinanes and Their Analogues: Synthesis of Lacinilene C, 2,7-Dihydroxycadalene, and Their Methyl Ethers

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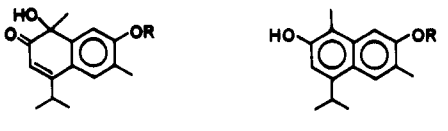
The total synthesis of lacinilene C methyl ether [1-hydroxy-4-isopropyl-7-methoxy-1,6-dimethyl-2(1*H*)-naphthalenone] has been accomplished in ten steps with an overall, optimal yield of 38% by starting with *o*-methylanisole. Formation of the key α-aryl-α-ketol functionality, which is particularly sensitive to oxidation, was accomplished by stepwise oxidation reactions based on the use of *N*-methylmorpholine *N*-oxide/osmium tetraoxide acting on alkene and trimethylsilyl enol ether functionality. Other oxidations could be accomplished by using dichlorodicyanobenzoquinone to generate unsaturation adjacent to the α-ketol group or to form substituted naphthalenes. These reactions permitted adjustment of the oxidation level and oxygenation pattern of the key intermediate, 7-methoxy-α-calacorene (3,4-dihydro-4-isopropyl-7-methoxy-1,6-dimethylnaphthalene), to accomplish the synthesis of 2-hydroxy-7-methoxycadalene, 2,7-dihydroxycadalene, 7-methoxycadalene, and 7-hydroxycadalene, in addition to lacinilene C and its methyl ether.

Of the numerous *Gossypium* secondary metabolites, the cadinane sesquiterpenoids comprise the largest group characterized to date.[1] Various members of this group reportedly possess interesting physiological activities, including action as phytoalexins,[2] as natural insect control substances,[3] and as a fraction of cotton dust which causes "brown lung disease".[4] While these biological activities provide a justification for development of approaches to the synthesis of these cadinanes, the generally high degree of oxygenation or novel oxygenation patterns provides synthetic problems which are of theoretical and practical interest. In this report we describe the synthesis of four related *Gossypium* cadinanes: lacinilene C (**1**), 2,7-dihydroxycadalene (**3**), and their methyl ethers, **2** and **4**, respectively.[5,6] Brief descriptions of our initial synthesis of **2** and those by two other groups have been published.[7-9]



1 R=H **3** R=H

2 R=Me **4** R=Me

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