Photochemical Reactions of *N*-Methylnaphthalene-2,3-dicarboximide with Alkenes

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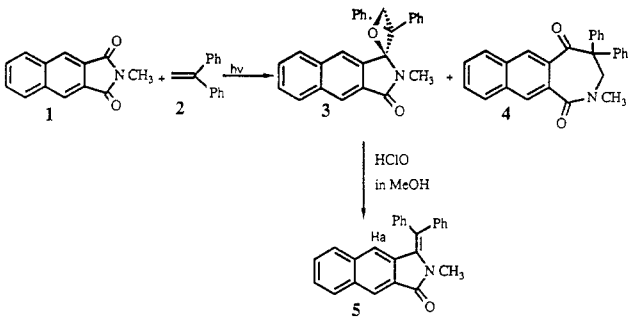
Previous studies have shown that *N*-methylphthalimide (NMP) reacts with alkenes to afford, in a few cases, oxetanes, along with products of alkene addition to the C(O)N bond and products arising from initial electron transfer. In this paper we explore the photochemistry of *N*-methylnaphthalene-2,3-dicarboximide (NMN). The photochemistry of NMN was studied in benzene, a solvent which we were unable to use with NMP due to solubility factors. In this solvent oxetanes were the major products found with several alkenes (α-methylstyrene, diphenylethylene, styrene, *trans*-stilbene). In the case of *trans*-stilbene a novel 2 + 2 addition to the 1,2-bond of NMN was also observed to give a photochemically labile cyclobutane. In benzene solvent alkene addition to the C(O)N bond was never a major product. Also investigated was a series of alkenes in acetonitrile containing methanol in which the expected products obtained by trapping the electron-transfer-generated radical anion radical cation pair with methanol were found. In the case of 2,3-dimethyl-2-butene there was observed a pair of photoreduction products analogous to those observed with this alkene and NMP. A study of solvent polarity effects on the ratio of these photoreduction products supports the previous suggestion that one of these arises via proton transfer followed by coupling of the radical pair, whereas the other comes from a rare case of radical cation–radical anion coupling followed by intramolecular proton transfer in the resultant zwitterion. Fluorescence quenching data for NMN with a series of unsaturated hydrocarbons are presented, and these data are shown to correlate well with the Weller equation.

In recent years the photochemistry of imides has been the subject to intensive investigation,[1] especially with respect to their reactions with alkenes where remarkable differences are found in the photoreactivity of alicyclic imides and arenedicarboximides (especially phthalimides). Aliphatic imides undergo efficient intra-[2] and intermolecular oxetane formation,[3] illustrating normal n,π^* carbonyl photoreactivity, whereas phthalimides undergo alcohol-incorporated C–C coupling at the carbonyl carbon (via electron transfer),[4] insertion of the alkene in the C(=O)—N bond of the imide moiety (dihydrobenzazepinedione formation),[5] and in a few cases oxetane formation.[6] Since most of the previous investigations have been confined to phthalimides there is little information on the effect of arene structure on the photochemistry of arenedicarboximides.[7] We focused our investigation on the elucidation of the effect of extended π-conjugation in the photochemistry of the imide system. Recent papers have reported on the photoreactions of three types of *N*-methylnaphthalenedicarboximides with alkenes in which the arene structure played a crucial role in determining the reaction pathways.[7] The predominant types of reaction of *N*-methyl-1,8- and *N*-methyl-1,2-naphthalenedicarboximides with alkenes in benzene were found to be cycloaddition to the aromatic C=C bond (cyclobutane formation) and insertion of alkene between the C(=O)—N bond of the imide moiety (dihydronaphthoazepinedione formation), respectively.[8] In methanol, *N*-methyl-1,8-naphthalenedicarboximide undergoes exclusive methanol–alkene addition to the aromatic ring, and no addition to the carbonyl group is observed. The purpose of this paper is to describe the details of the photoreaction of *N*-methylnaphthalene-2,3-dicarboximide (**1**, NMN) with a variety of alkenes. In con-

Scheme I



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(6) (a) Mazzocchi, P. H.; Minamikawa, S.; Bowen, M. *Heterocycles* **1978**, *9*, 1713. (b) Machida, M.; Takeuchi, H.; Kanaoka, Y. *Tetrahedron Lett.* **1982**, 4981. (c) Mazzocchi, P. H.; Klingler, L.; Edwards, M.; Wilson, P.; Shook, D. *Tetrahedron Lett.* **1983**, 143. (d) Mazzocchi, P. H.; Klingler, L. *J. Am. Chem. Soc.* **1984**, *106*, 7567.
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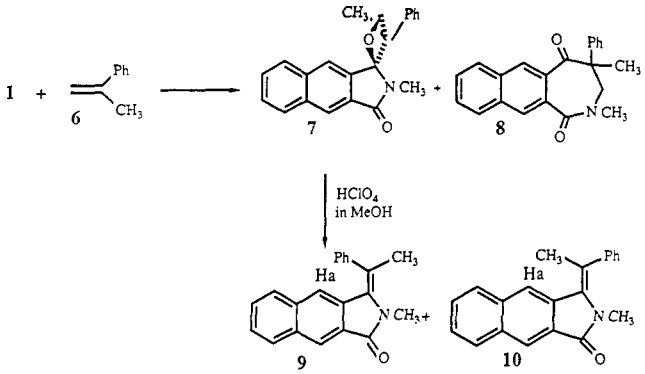
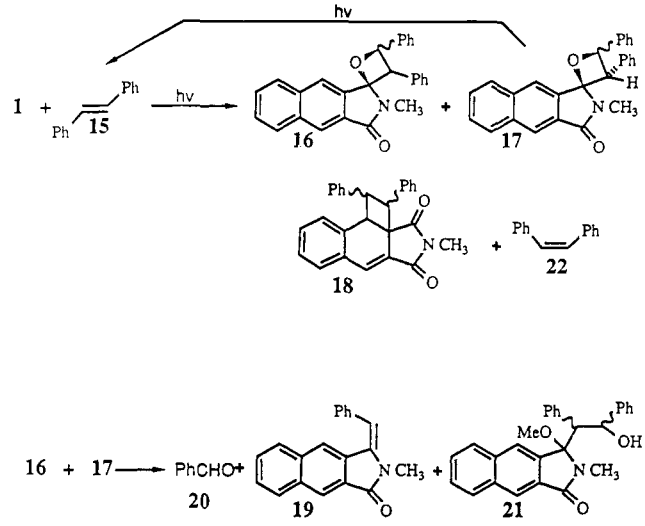
Scheme II



Scheme III



trast to other naphthalenedicarboximides, we have found that the addition of alkenes to the carbonyl C=O bond of the imide moiety (oxetane formation) is an important component of the reaction of **1** in benzene. Other reactions involving dihydronaphthoazepinedione formation, cyclobutane formation, and reactions initiated by electron transfer are also observed.

Results and Discussion

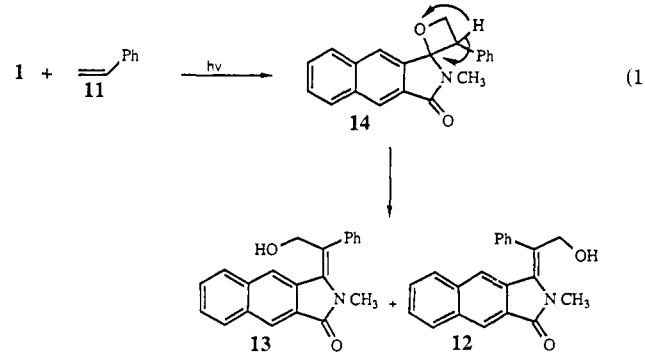
A solution of **1** and 1,1-diphenylethylene (**2**) in benzene was irradiated by light of >320 nm (aqueous $CuSO_4$ filter). After evaporation of the solvent, the residue was chromatographed on SiO_2 to give the oxetane **3** and dihydronaphthoazepinedione **4** (Scheme I). Since **3** was very sensitive to acid and was lost even on SiO_2 treatment, the isolated yields varied (0–50%) depending on the conditions in the separation. The yields of **3** and **4** were determined to be 78% and 12%, respectively, by integration of the ^1H NMR spectrum of the irradiation mixture containing an internal standard. The structure of **3** was assigned on the basis of the IR (a characteristic amide carbonyl band at 1705 cm^{-1}), ^1H NMR (oxetane methylene signals at δ 5.43 and 5.57, AB q, J = 7.0 Hz), mass spectra, elemental analysis, and chemical manipulation (acid decomposition); i.e., on treatment with a few drops of perchloric acid in methanol, **3** decomposed to give **5**. The structure of **4** was assigned on the basis of its spectral resemblance to the benzoanalogue obtained in the reaction of *N*-methylphthalimide (NMP) with **2**.[5c]

Irradiation of **1** and α-methylstyrene (**6**) in benzene gave similar results. Oxetane **7** was the major product (43%) and dihydronaphthoazepinedione **8** was the minor one (29%) (Scheme II). Acid decomposition of **7** in methanol afforded a mixture of **9** and **10**. The configuration of **9** and **10** was assigned on the basis of the ^1H NMR spectra. Thus, considerable shielding of NMe protons in the ^1H NMR of **10** at δ 2.72 and 2.77 and H_a in that of **9** at δ 7.32 was observed due to the anisotropic shielding effect from the eclipsing phenyl ring. Only one of the possible isomers of the oxetane was produced.

In the ^1H NMR spectrum of **7**, the chemical shift of the NMe signal (δ 2.55) is similar to that of the NMe signal of **3** (δ 2.66), rather than that of an oxetane possessing no phenyl substituents (**25**, δ 3.30, vide infra), probably due to the anisotropic shielding effect of the phenyl ring. On the other hand, the signal for H_a in **7** (δ 8.44 or 8.52) remains at lower field in analogy with that of the corresponding proton in **25** (δ 8.07 or 8.23) and in contrast with that of **3** (δ 7.6, in the aromatic multiplet at δ 6.9–8.0), where the proton seems to be shifted to higher field due to the anisotropic effect from the phenyl ring. These chemical shifts, together with the result of the acid decomposition, led to the assignment of the configuration of the oxetane ring shown (**3**).

Although a marked concentration dependency in the photoreaction of alkenes with *N*-methylphthalimide (NMP) on the ratio of the yield of oxetane to that of other types of products was reported,[6a,b] the ratio of the yields of **7**/**8** remained constant in the concentration region of 17–216 mM of **6**.

The reaction of **1** and styrene (**11**) in benzene was slow compared with its reaction with **2** and **6**; i.e., the relative rates for disappearance of **1** in solutions containing 10 mM of **1** and 100 mM of **2**, **6**, and **11** were in the ratio of 1:0.2:0.01. The major products were two alcohols (**12** and



(1)

13) presumably formed by hydrolytic decomposition of the oxetane precursor (**14**) (eq 1). The configuration of **12** and **13** was assigned on the basis of the chemical shifts of NMe protons in analogy with the assignments of **9** and **10**.

Irradiation of **1** and *trans*-stilbene (**15**) in benzene gave two oxetane stereoisomers (**16** and **17**) and one cyclobutane (**18**) (Scheme III). Acid decomposition of **16** or **17** in methanol afforded **19**, benzaldehyde (**20**), and a methanol adduct (**21**), although **16** and **17** were stable in methanol. The configuration of **19** was assigned on the basis of the shielding of the H_a proton (δ 7.74) in analogy with that of **9**. The structure of **21** was assigned on the basis of the doublet OH signal and the shielded OMe signal (δ 2.84 or 2.96) observed in the ^1H NMR spectrum. The alcohol is presumably produced by the addition of methanol to the tertiary carbonium ion stabilized by the amide nitrogen and β-naphthyl group. That **16** and **17** give the same methanol adduct (**21**) is interesting, indicating that the configurational relationship between the two phenyl substituents in **16** and **17** is the same and that the carbonium ion intermediate in both cases traps methanol preferentially to give a single diastereoisomer. The configuration at the 3′-carbon of the oxetane ring in **16** and **17** is easily

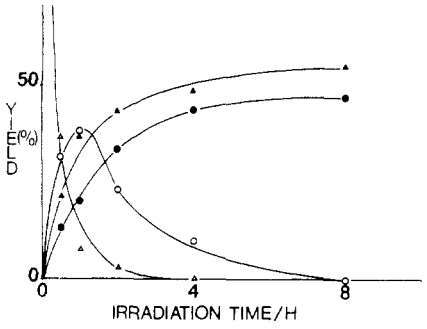


Figure 1. Yields of photoproducts from 1 + 15 in benzene as a function of time: (△) 1; (▲) 16; (●) 17; (○) 18.

assigned as shown on the basis of chemical shifts of the NMe and H_a signals in analogy with the assignment of that of 7.

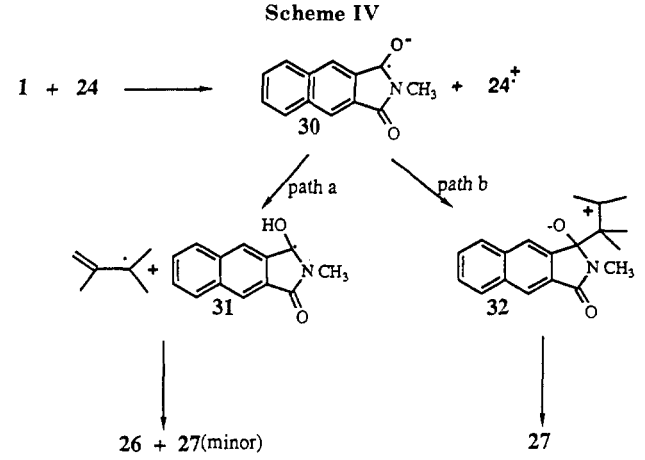
The cyclobutane structure of 18 was assigned largely on the basis of the three methine signals in the ^1H NMR spectrum. While 16 and 17 were photostable in benzene, 18 decomposed on irradiation (>320 nm) in benzene to 1 and 15. The photodecomposition to 15 may indicate a trans arrangement of the two phenyl substituents of the cyclobutane ring in 18. A similar photodecomposition to starting materials was observed in the cyclobutane produced by the photoaddition of alkenes to *N*-methylnaphthalene-1,8-dicarboximide.[8]

The yields of the photoproducts and of recovered 1 with time are shown in Figure 1, which shows that the yield of 18 decreases with increasing irradiation time after reaching the maximum, consistent with the observed competitive photodecomposition. The yield of *cis*-stilbene (22) was found to be 6% after 1 h of irradiation, when most of 1 had disappeared. Thus, the trans–cis isomerization of 15 was slow compared with the photoaddition. NMP (1) has a higher excited triplet energy (E_T = 60 kcal/mol) than that of 15 (E_T < 50 kcal/mol)[9] so that 15 would act as a typical triplet quencher of 1 and be isomerized to the cis isomer (22).[10] The photochemical results indicate that the trans–cis isomerization of 15 is slow compared with oxetane and cyclobutane formation and implies that if the reaction of 1 and 15 occurs from the triplet state of 1, it must occur at greater than the diffusion-controlled rate to give oxetane and cyclobutane or that these reactions occur from another excited state. We conclude that the oxetane and cyclobutane formation of 1 occurs directly from the reaction of the singlet excited state of 1 and the ground state of 15. The ratios of the yields of 16/17 and 16/18 at the early state of the photoreaction remained nearly constant in the concentration range of 14–417 mM of 15.

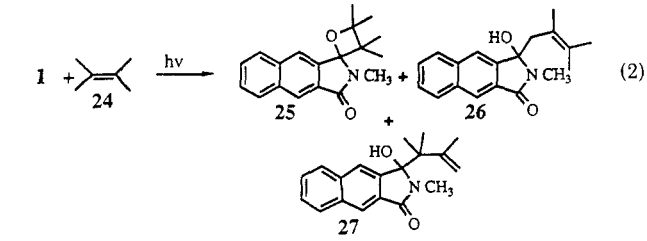
No products were observed in the photoreaction of 1 and 1-hexene, 4,4-dimethyl-1-pentene, or 2-methylpropane in benzene, although 2-methylpropene was reported to give products with NMP[5c] and isomeric *N*-methylnaphthalenedicarboximides,[8] indicating that 1 is less reactive than those systems with aliphatic alkenes. Photoreaction of 1 and 2-methyl-2-butene (23) in benzene gave a complex mixture of minor products from which we were not able to isolate any in pure form.

Electron-Transfer Chemistry. Irradiation of 1 and 2,3-dimethyl-2-butene (24) in benzene gave oxetane 25 and a pair of products (26 and 27) which could formally arise

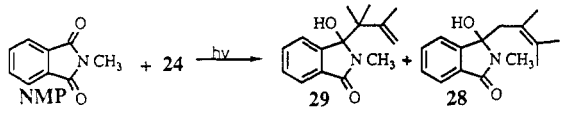
Scheme IV



by hydrogen abstraction by 1 followed by coupling of the resultant radical pair at either of the two allylic position on the 1,1,2-trimethylallyl radical (eq 2). The reaction



(2)



is analogous to that of NMP and 24, and the structure of products can be assigned on the basis of its spectral resemblance to the benzo analogues.[6d] It has now been established that this is an electron-transfer process in the phthalimide system[6d] and the absence of an isotope effect on the efficient fluorescence quenching of 2,3-naphthalimide using 2,3-dimethyl-2-butene or 2,3-dimethyl-2-butene-d_{12} indicates that the electron-transfer mechanism holds in this system also.[6d] However, there is some question concerning the events succeeding the initial electron transfer. One scenario (Scheme IV) has the radical cation transferring a proton to the radical anion (path a), giving a radical pair (31), one of which is the 1,1,2-trimethylallyl radical. Coupling of the allyl radical at each of the nonequivalent positions gives the observed products in this "radical coupling mechanism".[11] An alternate scheme has this allyl radical coupling preferentially at its less hindered position to give 26 on the basis of kinetic and thermodynamic considerations. Radical ion pair coupling (Scheme IV, path b) is proposed to take place to give zwitterion 32, which undergoes proton transfer to give 27 as the only product in what we call the "zwitterion mechanism".[5c,12] We present here several pieces of data which are relevant to this question and support the latter mechanism.

We reasoned that the solvent polarity should have little or no effect on the position of coupling of an allyl radical; i.e., the product-determining step in the radical coupling

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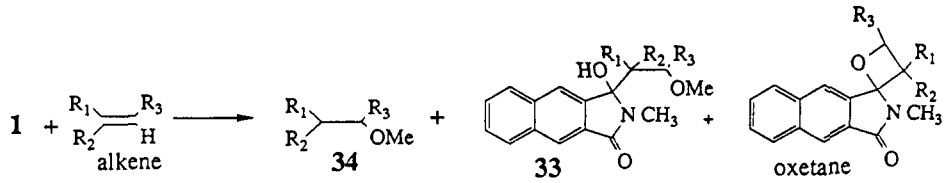
(10) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1973; Vol. 3, p 1.
(11) Mattes, S. L.; Farid, S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233.
(12) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609.

Table I. Yields of Photoproducts from 1 and Alkenes in Methanol-Acetonitrile (2:1 v/v)



					yield,[a] %				
					33			oxetane	
R^1	R^2	R^3	alkene	[alkene], mM			34		
Ph	Ph	H	2	152	**33a**	47	71	3	10
Ph	Me	H	6[b]	282	**33b**	80			
Ph	H	Ph	15	185	**33c**	83			
Me	Me	Me	23	571	**33d**	79			

[a] Yields were based on consumed imide. [b] In 1:10 MeOH–MeAc we observe **33b** and 8 in 6:1 ratio by HPLC.

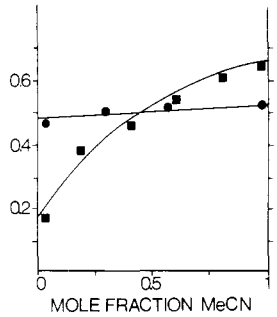
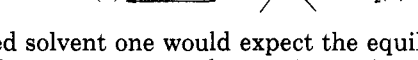


Figure 2. Plot of the ratio of yields of products from reaction of 1 (NMN) + 24 and NMP + 24 as a function of the mole fraction of acetonitrile: (■) 27/(26 + 27); (●) 29/(28 + 29).

mechanism should be solvent polarity independent. That should not be the case in the zwitterion mechanism where increases in solvent polarity should stabilize the zwitterion intermediate and thus the product ratio should change with the terminal of olefin **27** becoming dominant.

We first investigated the NMP system and found a small but real solvent effect favoring the terminal olefin **29** in polar solvents (Figure 2). Examination of the 2,3-NMN system was rewarding in that it showed (Figure 2) a very large solvent effect. We considered that this apparent solvent polarity effect might really be the result of the increased basicity of methyl acetate over acetonitrile and more efficient deprotonation of **32** in the less polar solvent. Apaprently, there is some validity to this contention since the **27**/(**26** + **27**) ratio is smaller in methyl acetate (0.17) than it is in the less polar benzene (**27**/(**26** + **27**) ratio = 0.25 in benzene) although the still significant decrease in this ratio in benzene vs. acetonitrile indicates that the major effect must be due to solvent polarity and not solvent basicity. We assume that methyl acetate may assist in deprotonating the radical cation, although we believe that the imide radical anions should be the most effective actors in this regard. Thus product distributions in systems with different electron acceptors and therefore different radical anions with different basicities should yield different product ratios as radical cation deprotonation occurs in the contact ion pair. Solvent basicity would be expected to have a variable effect depending on the basicity of the radical anion involved.

One possibility that could complicate this interpretation is that an equilibrium might exist between the radical cation and allyl radical which could affect product distribution.[13] The situation is outlined in eq 3 for the 2,3-dimethyl-2 butene system, and we investigated this possibility by examining solvent isotope effects. In a



(3)

deuterated solvent one would expect the equilibrium to be skewed to the right since deuteration of the allyl radical should be less efficient than protonation. We found that the product distribution of alkenes in the NMP system in MeOD was identical with that in MeOH. In deuterioacetonitrile we found a small isotope effect (~10%) but in the wrong direction; i.e., the terminal olefin was favored as if equilibrium had been shifted to the left. This small change might be ascribed to small increases in solvent basicity[14] or solvent polarity (vide infra). These results establish that, at least in the imide system, this equilibrium cannot be important. Importantly, in the case of NMP and 2,3-NMN, studies using naphthalene as the electron-transfer sensitizer unequivocally demonstrated that the photoreduction products (**26** and **27**) are formed from a contact ion pair rather than separated ions.[15]

We believe that these experiments favor the zwitterionic mechanism previously proposed over the radical coupling mechanism for the formation of **27** and **29**.

A typical photochemical electron-transfer reaction of phthalimides is alcohol-incorporated C–C coupling with alkenes.[4] Thus, we investigated the reaction of 1 and several alkenes in methanol–acetonitrile. Irradiation of a mixture of 1 and 2 in methanol–acetonitrile (1/2 v/v) gave a methanol-incorporated adduct at the carbonyl carbon (**33a**) together with 2,2-diphenylethyl methyl ether (**34**) and the oxetane **3**. The results of the reactions of 1 and alkenes **6**, **15**, and **23** are summarized in Table I and indicate that the methanol-incorporated addition at the carbonyl carbon is a characteristic reaction for 1. In the case of **6** we observe 8 along with **33a** in a 1:6 ratio in a 1:10 MeOH–MeOAc solvent mixture by HPLC analysis. However, no methanol-incorporated adducts were obtained with 2-methylpropene and 1-hexene, although reactions of NMP and 2-methylpropene gave the corresponding adduct.[4b,c]

A possible mechanism for the methanol-incorporated photoaddition of 1 and 2 is shown in Scheme V, in analogy with that of phthalimides and alkenes.[4] The initial step of the reaction is an electron-transfer process from **2** to the singlet excited state of 1. Since compound **34** is a typical product from electron-transfer photosensitized reactions, as reported by Arnold and co-workers,[16] it appears that

(13) Borg, R. M.; Arnold, D. R.; Cameron, T. S. *Can. J. Chem.* **1984**, *62*, 1785.

(14) The arguement can be made that deuterioacetonitrile is a weaker base than acetonitrile.

(15) Klinger, L. Ph.D. Thesis, University of Maryland, 1984.

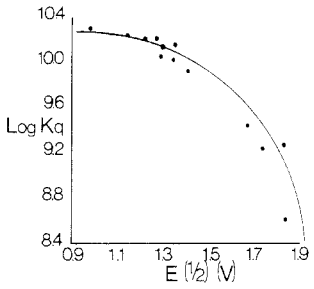
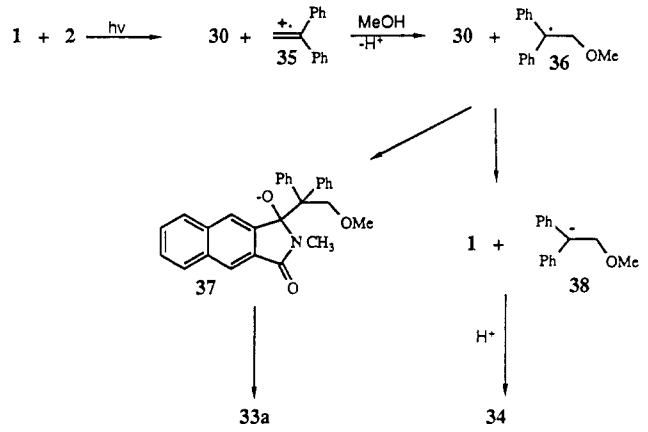


Figure 3. Plot of log k_q vs. $E_{1/2}$ for fluorescence quenching of 1 (NMN). The solid line represents theoretical values predicted from the Weller equations. The points are experimental values (see Table II).

Scheme V



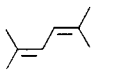
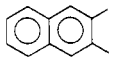
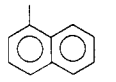
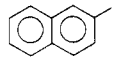
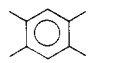
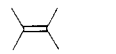
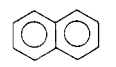
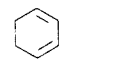
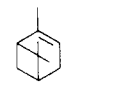
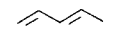
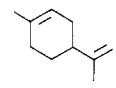
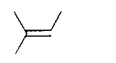
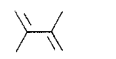
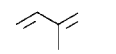
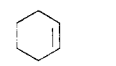
34 and **33a** arise from the radical **36** which can either couple with **30** to give **33a** or be reduced by back electron transfer from **30** to give **38** and thus **34** as outlined in Scheme V.

The free-energy change associated with the photochemical electron transfer (ΔG_{et}) of 1 with a series of alkenes can be roughly estimated by using eq 4.[17] In the equation,

$$\Delta G_{et} = 23.06[E(D/D^+) - E(A^-/A)] - E_{0,0} \quad (4)$$

$E(D/D^+)$ is the oxidation potential of alkenes, $E(A^-/A)$ is the reduction potential of 1 (−1.60 V in 0.5 M Et_4NClO_4/acetonitrile vs. SCE), and $E_{0,0}$ is the singlet excitation energy of 1 (79 kcal/mol from the absorption and fluorescence spectra). A compilation of fluorescence quenching data and oxidation potential data for a series of donors with 2,3-NMN is shown in Table II. The fit between the experimental and calculated data is excellent as shown in Figure 3 and Table II.

Table II. Experimental and Theoretical Constants for the Fluorescence Quenching of NMN by Potential Electron Donors

	IP, eV	$E_{+1/2}$, V	ΔG, kcal/mol	calcd k_q × 10^{-10}	exptl k_q × 10^{-10}
	7.84[18]	0.98[23]	−18.35	1.41	2.06
	7.81[19]	1.14[24]	−16.51	1.38	1.73
	7.96[20]	1.22[25]	−12.82	1.31	1.52
	7.95[20]	1.24[25]	−12.36	1.30	1.53
	8.17[20]	1.27[23]	−11.66	1.28	1.59
	8.03[20]	1.29[25]	−11.20	1.27	1.13
	8.30[20]	1.30[26]	−10.97	1.26	1.46
	8.12[20]	1.34[25]	−10.05	1.23	1.02
	8.30[21]	1.35[23]	−9.82	1.22	1.45
	8.39[18]	1.41[19]	−8.44	1.16	0.827
	8.59[21]	1.63[23]	−3.36	0.653	1.09
	8.62[18]	1.67[27]	−2.44	0.500	0.269
	8.67[20]	1.73[26]	−10.6	0.265	0.175
	8.72[21]	1.83[25]	1.25	0.0397	0.183
	8.85[21]	1.84[25]	1.48	0.0309	0.0423
	8.95[22]	1.98[22]	4.71	0.00432	0

Our experimental results are consistent with expectations that the methanol-incorporated addition occurs only in the cases where electron transfer is exothermic.

The calculated ΔG_{et} values for **2**, **23**, 2-methylpropene, and 1-hexene with **1** are −8.28, −1.15, 12.7, and 18.5 kcal/mol, respectively. The values used for the oxidation potentials were as follows: **2**, 1.48 V;[28] **23**, 1.79 V;[4c] 2-methylpropene, 2.39 V;[4c] 1-hexene, 2.64 V.[4c]

In summary, we have found alkenes add efficiently to the C=O bond of **1** in benzene to form oxetanes in competition with addition to afford dehydronaphthazepinediones and electron-transfer processes. The extent of each of these reactions depends upon the structure of the alkene and solvent properties. Thus, alkenes of low ionization potential preferentially undergo electron transfer to give photoreduction (hydrogen abstraction) and methanol-incorporated adducts.

One of the major findings of this research is that **1** undergoes oxetane formation with alkenes much more efficiently than any of the other arenedicarboximides previously studied. One possible reason for this discrepancy

(16) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080.
(17) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(18) Labianca, D. A.; Taylor, G. N.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 3679.
(19) *Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions*; Franklin, J. L., Dillard, J. G., Rosenstock, H. M., Herron, J. T., Draxl, K., Field, F. H., Eds.; National Bureau of Standards: Washington, DC, 1969.
(20) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.
(21) Borkent, J. H.; Verhoeven, J. W.; de Boer, Th. J. *Tetrahedron Lett.* **1972**, *32*, 3363.
(22) Foffani, A.; Piganataro, S.; Cantone, B.; Grasso, F. *Z. Phys. Chem. Neue Folge* **1964**, 42, 221.
(23) The value was interpolated from correlation of the literature ionization potentials (IP) vs. the literature oxidation potentials $E_{+1/2}$ using the literature oxidation potential. Values for alkenes are included in the correlation.
(24) The literature ionization potential was used to interpolate the $E_{+1/2}$ from a correlation of IP vs. $E_{+1/2}$. Values for dienes are included in the correlation.
(25) Shono, T.; Ikeda, A. *J. Am. Chem. Soc.* **1972**, *94*, 7893.
(26) The literature IP was used to interpolate $E_{+1/2}$ from a correlation of IP vs. $E_{+1/2}$ for aromatic compounds.
(27) (a) Neikam, W. C.; Dimelar, G. R.; Desmond, M. M. *J. Electrochem. Soc.* **1964**, *111*, 1190.
(28) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931.

may be that the lowest excited state of 1 is π,π^* (79 kcal/mol) with an energetically proximate n,π^* state of slightly higher energy. The energetic relationships for N-methylphthalimide are approximately the same except that the situation is reversed with the n,π^* (80 kcal/mol) state at lower energy.[29] The result is that the excited state of 1 is π,π^* with some, n,π^* mixed in rather than the reverse, and this difference may be reflected in the significant change in reactivity.

The second major result is that solvent and isotope studies have furnished major support for the proposition that radical cation–radical anion pairs can undergo radical coupling followed by proton transfer in competition with proton transfer followed by radical coupling. The dramatic change in product ratios in more polar solvents cannot be rationalized by a mechanism that only involves coupling of neutrals (radicals) but can be nicely explained by a mechanism that involves the coupling of neutrals and ions.

Experimental Section

Melting points are uncorrected. Chemical shifts are reported in ppm (δ) relative to internal $SiMe_4$. UV irradiations was carried out with an Eikosha PIH 300-W high-pressure Hg lamp through an aqueous $CuSO_4$ filter of about 1-cm thickness (>320 nm) under N_2 at ambient temperature or with a Hanovia 450-W lamp through Pyrex. Column chromatography was done on Wakogel C-200 (silica gel, 74–149 μm).

Corrected fluorescence spectra were recorded on a Perkin-Elmer MPF-44B fluorescence spectrophotometer equipped with a DCSU-1 correction unit. Fluorescence quenching data were obtained on a Perkin-Elmer Model 204 fluorescence spectrophotometer.

Materials. N-Methylnaphthalene-2,3-dicarboximide (1, NMN) was prepared as follows. A solution of 5 g of commercially available naphthalene-2,3-dicarboxylic acid in 30 mL of acetic anhydride was refluxed for 10 min, and the solvent was then removed in vacuo. To the residue was added 20 mL of aqueous methylamine (40%), and the solution was gently warmed for 1 h. After removal of the solvent in vacuo, a solution of the residue in 20 mL of acetic anhydride was refluxed for 10 min, and the solvent was removed in vacuo. The crude product was purified by column chromatography (chloroform eluant) and recrystallized from chloroform–ethanol to give 3.7 g (69%) of pure 1: mp 215–217 °C; ^{1}H NMR ($CDCl_3$) 3.17 (s, 3 H), 7.5–7.7 (m, 2 H), 7.8–8.1 (m, 2 H), 8.19 (s, 2 H). Anal. Calcd for $C_{13}H_{21}NO_2$: C, 73.92; H, 4.30; N, 6.63. Found: C, 74.05; H, 4.34; N, 6.61.

Alkenes **2**, **6**, **11**, **15**, **21**, **23**, and **24** were commercially available and purified by recrystallization or distillation.

Irradiation of 1 with 2 in Benzene. A solution of 53 mg (10 mM) of 1 and 450 mg (100 mM) or 2 in 25 mL of benzene was irradiated for a period of 8 h. Solvent was removed by evaporation and the residue was chromatographed (eluant dichloromethane–ether) to give 3 and 4. Since 3 was sensitive to acid (silica gel) a rapid separation was required. The yields of the products were determined by integration of the ^{1}H NMR spectrum of the reaction mixture with internal standard (stilbene-α,β-diol diacetate) to give 78% (3) and 12% (4).

2-Methyl-3′,3′-diphenylspiro[1*H*-benz[*f*]isoindole-1,2′-oxetan]-3(2*H*)-one (3): mp 182–185 °C; ^{1}H NMR ($CDCl_3$) 2.66 (s, 3 H), 5.43 and 5.57 (AB q, J = 7.0 Hz, 2 H), 6.9–8.0 (m, 15 H), 8.24 (s, 1 H); IR (KBr) 1705, 1570, 962, 700 cm^{-1}; MS (20 eV), m/e (relative intensity) 391 (M^+, 2), 361 ($M^+ - H_2O$, 100). Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found: C, 83.02; H, 5.69; N, 3.29.

2-Methyl-4,4-diphenyl-3,4-dihydro-1*H*-naphtho[3,2-*c*]azepine-1,5(2*H*)-dione (4): mp 92–95 °C; ^{1}H NMR ($CDCl_3$) 2.42 (s, 3 H), 4.28 (br s, 2 H), 7.0–8.1 (m, 14 H), 7.76 (s, 1 H), 8.46 (s, 1 H); IR (KBr) 1693, 1655, 1498, 1452, 1275, 704 cm^{-1}. Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found: C, 83.11; H, 5.58; N, 3.43.

Acid Decomposition of 3. To a solution of 50 mg of 3 in 20 mL of methanol was added a few drops of perchloric acid, the mixture was allowed to stand for 1 day, and then 30 mL of chloroform was added. The solution was washed with water, dried over magnesium sulfate and solvent removed by evaporation. The residue was chromatographed (dichloromethane eluant) to give 5 (39 mg, 84%).

2-Methyl-3-(diphenylmethylene)-1*H*-benz[*f*]isoindol-3(2*H*)-one (5): mp 256–258.5 °C (from benzene–ethanol); ^{1}H NMR ($CDCl_3$) 2.94 (s, 3 H), 6.82 (s, 1 H), 7.2–7.6 (m, 13 H), 7.8–8.1 (m, 1 H), 8.39 (s, 1 H); IR (KBr) 1704, 1364, 1116, 1015, 748, 704 cm^{-1}. Anal. Calcd for $C_{26}H_{19}NO$: C, 86.40; H, 5.30; N, 3.88. Found: C, 86.26; H, 5.32; N, 3.85.

Irradiation of 1 with 6 in Benzene. A solution of 53 mg (10 mM) of 1 and 295 mg (100 mM) of 6 in 25 mL of benzene was irradiated for 2 days. The solvent was removed by evaporation and the residue was chromatographed (dichloromethane–ether eluant) to give 7 and 8. The yields of the products were determined by integration of the ^{1}H NMR spectrum of the reaction mixture with internal standard (stilbene-α,β-diol diacetate) to be 43% (7) and 29% (8). The stereoisomer of the oxetane 7 could not be observed in the ^{1}H NMR spectrum.

2,3′-Dimethyl-3′-phenylspiro[1*H*-benz[*f*]isoindole-1,2′-oxetan]-3(2*H*)-one (7): mp 162–165 °C; ^{1}H NMR ($CDCl_3$) 1.78 (s, 3 H), 2.55 (s, 3 H), 4.62 and 5.37 (AB q, J = 5.5 Hz, 2 H), 6.7–7.0 (m, 2 H), 7.1–8.1 (m, 7 H), 8.35 (s, 1 H), 8.38 (s, 1 H); IR (KBr) 1703, 1422, 1371, 1049, 963, 701 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.45; H, 6.03; N, 4.19.

2,4-Dimethyl-4-phenyl-3,4-dihydro-1*H*-naphth[3,2-*c*]azepine-1,5(2*H*)-dione (8): mp 72–74 °C; ^{1}H NMR ($CDCl_3$) 1.69 (s, 3 H) 2.96 (s, 3 H), 3.67 and 3.96 (AB q, J = 14.2 Hz, 2 H), 7.1–7.4 (m, 4 H), 7.5–7.7 (m, 2 H), 7.8–8.1 (m, 1 H), 8.04 (s, 1 H), 8.51 (s, 1 H); IR (KBr) 1686, 1652, 1485, 1402, 1273, 766, 704 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 79.92; H, 5.87; N, 4.07.

Acid Decomposition of 7. This reaction was carried out on 50 mg of 7 in a manner identical with that used for 3 to give a mixture of 9 and 10 [28 mg (62%), 9/10 = 1:0.44]. The mixture was crystallized from ether–hexane (1:2 v/v).

A mixture of (*E*)-2-methyl-3-(1-phenylethylidene)-1*H*-benz[*f*]isoindol-3(2*H*)-one (9) and its *Z* isomer (10) [9/10 = 1:1]: mp 150–168 °C; ^{1}H NMR ($CDCl_3$) [9] 2.56 (s, 3 H), 3.74 (s, 3 H), 7.1–8.2 (m, 9 H), 7.32 (s, 1 H), 8.39 (s, 1 H), [10] 2.72 (s, 3 H), 2.77 (s, 3 H), 7.1–8.2 (m, 9 H), 8.44 (s, 1 H), 8.52 (s, 1 H); IR (KBr) 1698, 1631, 1427, 1362, 751, 703 cm^{-1}. Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.54; H, 5.44; N, 4.81.

Irradiation of 1 with 11 in Benzene. A solution of 53 mg (10 mM) of 1 and 260 mg (100 mM) of 11 in 25 mL of benzene was irradiated for 8 days. Solvent was removed by evaporation and the residue was chromatographed (dichloromethane–ether eluant) to give 12 (32 mg, 40%) and 13 (22 mg, 28%).

(*Z*)-3-(2-Hydroxy-1-phenylethylidene)-2-methyl-1*H*-benz[*f*]isoindol-3(2*H*)-one (12): mp 200–203 °C; ^{1}H NMR ($CDCl_3$) 3.76 (s, 3 H), 4.81 (s, 3 H), 6.44 (s, 1 H), 7.3–7.7 (m, 9 H), 7.8–8.1 (m, 1 H), 8.35 (s, 1 H); IR (KBr) 3320, 1678, 1612, 1367, 1004, 715 cm^{-1}. Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.22; H, 5.59; N, 4.34.

(*E*)-3-(2-Hydroxy-1-phenylethylidene)-2-methyl-1*H*-benz[*f*]isoindol-3(2*H*)-one (13): mp 197–199 °C; ^{1}H NMR ($CDCl_3$) 2.76 (s, 3 H), 5.07 (s, 2 H), 6.40 (s, 1 H), 7.2–8.2 (m, 9 H), 8.49 (s, 1 H), 8.65 (s, 1 H); IR (KBr) 3430, 1715, 1648, 1497, 1455, 703 cm^{-1}. Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98, H, 5.43; N, 4.44. Found: C, 80.14; H, 5.65; N, 4.31.

Irradiation of 1 with 15 in Benzene. A solution of 50 mg (16 mM) of 1 and 500 mg (185 mM) of 15 in 15 mL of benzene was irradiated for 2 h. The solvent was removed by evaporation and the residue chromatographed (dichloromethane–ether eluant) to give 16–18. The yields of the products determined by integration of the ^{1}H NMR spectrum of the reaction mixture with internal standard are shown in Figure 1.

One isomer of 2-methyl-3′,4′-diphenylspiro[1*H*-benz[*f*]isoindole-1,2′-oxetan]-3(2*H*)-one (16): mp 178–180 °C; ^{1}H NMR ($CDCl_3$) 2.88 (s, 3 H), 5.02 and 6.42 (AB q, J = 8.7 Hz, 2 H), 6.9–8.2 (m, 14 H), 8.25 (s, 1 H), 8.41 (s, 1 H); IR (KBr) 1705, 1390, 1368,

(29) Coyle, J. D.; Newport G. L. *J. Chem. Soc., Perkin Trans. 2* **1978**, 133.

(30) Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *100*, 5806. Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499.

962, 766, 702 cm^{-1}. Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found: C, 83.05; H, 5.48; N, 3.49.

Another isomer of 2-methyl-3′,4′-diphenylspiro[1*H*-benz[*f*]-isoindole-1,2′-oxetan]-3(2*H*)-one (**17**): mp 165–169 °C; ^{1}H NMR ($CDCl_3$) 3.29 (s, 3 H), 4.98 and 6.42 (q, J = 8.5 Hz), 6.9–8.1 (m, 14 H), 7.70 (s, 1 H), 8.34 (s, 1 H); IR (KBr) 1698, 1382, 1360, 964, 758, 696 cm^{-1}. Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found: C, 83.12; H, 5.53; N, 3.37.

2-Methyl-10,11-diphenyl-3a,4-ethano-3a,4-dihydrobenz[*f*]isoindole-1,3(2*H*)-dione (**18**): mp 86–88 °C; ^{1}H NMR ($CDCl_3$) 2.85 (s, 3 H), 3.57 (dd, J = 7.0, 10.3 Hz, 1 H), 4.22 (d, J = 10.3 Hz, 1 H), 4.26 (d, J = 7.0 Hz, 1 H), 6.7–7.5 (m, 15 H); IR (KBr) 1773, 1718, 1432, 1378, 762, 704 cm^{-1}. Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found: C, 82.71; H, 5.49; N, 3.40.

Acid Decomposition of 16 and 17. This reaction was carried out on 100 mg of **16** in the manner described for **3** to give **19** (29 mg, 40%), **20** (12 mg, 44%), and **21** (19 mg, 18%).

Acid decomposition of **17** (50 mg) as described above gave **19** (21 mg, 58%), **20** (7 mg, 52%), and **21** (4 mg, 7%).

(*E*)-2-Methyl-3-(phenylmethylene)-1*H*-benz[*f*]isoindol-3-(2*H*)-one (**19**): mp 212–215 °C; ^{1}H NMR ($CDCl_3$) 3.33 (s, 3 H), 6.39 (s, 1 H), 6.9–8.0 (m, 9 H), 7.74 (s, 1 H), 8.31 (s, 1 H); IR (KBr) 1707, 1648, 1392, 1104, 896, 782, 738 cm^{-1}. Anal. Calcd for $C_{20}H_{15}NO$: C, 84.18; H, 5.30; N, 4.91. Found: C, 83.96; H, 5.18; N, 4.85.

3-(2-Hydroxy-1,2-diphenylethyl)-3-methoxy-2-methyl-1*H*-benz[*f*]isoindol-3(2*H*)-one (**21**): mp 176–179 °C; ^{1}H NMR ($CDCl_3$) 2.84 (s, 3 H), 2.96 (s, 3 H), 3.60 (d, J = 10.5 Hz, 1 H), 5.29 (dd, J = 2.0, 10.5 Hz, 1 H), 5.76 (d, J = 2.0 Hz, 1 H), 6.0–6.3 (m, 2 H), 6.6–7.3 (m, 8 H), 7.6–7.9 (m, 2 H), 8.0–8.3 (m, 2 H), 8.37 (s, 1 H), 8.68 (s, 1 H); IR (KBr) 3430, 1695, 1428, 1395, 1064, 768 cm^{-1}. Anal. Calcd for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.27; H, 6.12; N, 3.30.

Irradiation of 1 with 24 in Benzene. A solution of 53 mg (10 mM) of **1** and 210 mg (100 mM) of **24** in 25 mL of benzene was irradiated for 3 h. The solvent was removed by evaporation and the residue was chromatographed (dichloromethane–ether eluant) to give **25–27**. The yields of the products determined by integration of the ^{1}H NMR spectrum of the reaction mixture with an internal standard were 21% (**25**), 49% (**26**), and 16% (**27**).

Photolyses of 53 mg (10 mM) of **1** and 210 mg (100 mM) of **24** were performed in mixtures of ethyl acetate and acetonitrile (25 mL). The yields of the product were determined by integration of the ^{1}H NMR spectra. The results are shown in Figure 2.

2,3′,3′,4′,4′-Pentamethylspiro[1*H*-benz[*f*]isoindole-1,2′-oxetan]-3(2*H*)-one (**25**): oil; ^{1}H NMR ($CDCl_3$) 1.04 (s, 3 H), 1.25 (s, 3 H), 1.56 (s, 3 H), 1.71 (s, 3 H), 3.30 (s, 3 H), 7.4–7.7 (m, 2 H), 7.8–8.0 (m, 2 H), 8.07 (s, 1 H), 8.23 (s, 1 H); IR (oil) 2960, 1705, 1372, 1043, 786, 759 cm^{-1}. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.56; H, 7.44; N, 4.49.

3-Hydroxy-2-methyl-3-(2,3-dimethyl-2-butenyl)spiro[1*H*-benz[*f*]isoindole-1,2′-oxetan]-3(2*H*)-one (**26**): mp 174–177 °C; ^{1}H NMR (CD_3SOCD_3) 1.26 (s, 3 H), 1.42 (s, 6 H), 2.60 and 2.86 (AB q, J = 14 Hz, 2 H), 2.87 (s, 3 H), 6.20 (s, 1 H), 7.4–7.6 (m, 2 H), 7.86 (s, 1 H), 7.8–8.0 (m, 2 H), 8.08 (s, 1 H); IR (KBr) 3270, 1665, 1433, 1401, 1077, 754, 480 cm^{-1}. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.34; H, 7.10; N, 4.68.

3-Hydroxy-2-methyl-3-(1,1,2-trimethyl-2-propenyl)-1*H*-benz-[*f*]isoindol-3(2*H*)-one (**27**): mp 143–146 °C; ^{1}H NMR ($CDCl_3$) 1.03 (s, 3 H), 1.08 (s, 2 H), 1.97 (s, 3 H), 2.85 (s, 3 H), 4.07 (s, 1 H), 4.61 (br s, 1 H), 4.88 (br s, 1 H), 7.0–7.7 (m, 4 H), 7.77 (s, 1 H), 7.87 (s, 1 H); IR (KBr) 3280, 1698, 1432, 1396, 1074, 770, 486 cm^{-1}. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.23; H, 7.07; N, 4.72.

Irradiation of 1 with 2 in Methanol–Acetonitrile. A solution of 100 mg (19 mM) of **1** and 684 mg (152 mM) of **2** in 25 mL of a mixture of methanol–acetonitrile (1/2 v/v) was irradiated for 3 h. The solvent was removed by evaporation, and the residue was chromatographed (dichloromethane–ether eluant) to give **33a** (71 mg, 71%), **34** (94 mg, 47%), and **3** (19 mg, 10%). 2,2-Diphenylethyl methyl ether (**34**) was identical with a sample prepared by irradiation of **2**, *p*-dicyanobenzene, and phenanthrene (sensitizer) in methanol.[15]

3-Hydroxy-3-(2-methoxy-1,1-diphenylethyl)-2-methyl-1*H*-benz[*f*]isoindol-3(2*H*)-one (**33a**): mp 214–216 °C; ^{1}H NMR (CD_3SOCD_3) 2.69 (s, 3 H; 3.11 in $CDCl_3$), 3.09 (s, 3 H; 3.31 in $CDCl_3$), 4.54 and 4.70 (AB q, J = 9 Hz, 2 H), 7.0–8.1 (m, 17 H); IR (KBr) 3220, 1675, 1396, 1120, 758, 718 cm^{-1}. Anal. Calcd for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.70; H, 6.24; N, 3.03.

Irradiation of 1 and 6 in Methanol–Acetonitrile. A solution of 100 mg (19 mM) of **1** and 832 mg (282 mM) of **6** in 25 mL of a mixture of methanol–acetonitrile (1/2 v/v) was irradiated for 3 h. The solvent was removed by evaporation, and the residue was chromatographed (dichloromethane–ether eluant) to give **33b** (137 mg, 80%).

A mixture of diastereomers (1:1) of 3-hydroxy-3-(2-methoxy-1-methyl-1-phenylethyl)-2-methyl-1*H*-benz[*f*]isoindol-3(2*H*)-one (**33b**): mp 163–172 °C; ^{1}H NMR ($CDCl_3$) 1.17 (s, 3 H), 1.51 (s, 3 H), 2.82 (s, 3 H), 3.06 (s, 3 H), 3.45 (s, 6 H), 3.68 and 3.89 (AB q, J = 8.7 Hz, 2 H), 3.90 and 3.98 (AB q, J = 7.5 Hz, 2 H), 5.12 (s, 1 H), 5.38 (s, 1 H), 6.66 (s, 1 H), 7.1–7.9 (m, 19 H), 7.99 (s, 1 H), 8.05 (s, 1 H); IR (KBr) 3120, 1675, 1386, 1103, 1054, 745, 698 cm^{-1}. Anal. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.41; H, 6.26; N, 3.76.

When the same reaction was carried out in a 1:10 mixture of methanol–methyl acetate, a 6:1 ratio of **33b** and **8** was observed by HPLC analysis.

Irradiation of 1 with 15 in Methanol–Acetonitrile. A solution of 100 mg (19 mM) of **1** and 833 mg (185 mM) of **15** in 25 mL of a mixture of methanol–acetonitrile (1/2 v/v) was irradiated for 3 h. The solvent was removed by evaporation, and the residue was chromatographed (dichloromethane–ether eluant) to give **33c** (166 mg, 83%). Recrystallization of the oily products (**33c**) from benzene–ethanol gave one diastereomer.

Main diastereomer of 3-hydroxy-3-(2-methoxy-1,2-diphenylethyl)-2-methyl-1*H*-benz[*f*]isoindol-3(2*H*)-one (**33c**): mp 183–185 °C; ^{1}H NMR (CD_3SOCD_3) 3.05 (s, 3 H), 3.19 (s, 3 H), 5.08 and 5.58 (AB q, J = 4 Hz, 2 H), 6.60 (s, 1 H), 6.99 (s, 1 H), 7.1–7.8 (m, 13 H), 7.9–8.2 (m, 1 H), 8.14 (s, 1 H); IR (KBr) 3250, 1680, 1438, 1402, 1066, 753, 708 cm^{-1}. Anal. Calcd for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.63; H, 6.25; N, 3.04.

Irradiation of 1 with 23 in Methanol–Acetonitrile. A solution of 100 mg (19 mM) of **1** and 999 mg (571 mM) of **23** in 25 mL of a mixture of methanol–acetonitrile (1/2 v/v) was irradiated for 3 h. The solvent was removed by evaporation, and the residue was chromatographed (dichloromethane–ether eluant) to give **33d** (diastereomer A, 62 mg, 42%; diastereomer B, 55 mg, 37%).

Diastereomer A of 3-hydroxy-3-(2-methoxy-1,1,2-trimethylethyl)-2-methyl-1*H*-benz[*f*]isoindol-3(2*H*)-one (**33d**): mp 126–129 °C; ^{1}H NMR ($CDCl_3$) 0.47 (s, 3 H), 1.13 (d, 3 H), 1.34 (s, 3 H), 3.10 (s, 3 H), 3.36 (s, 3 H), 3.74 (q, 1 H), 6.42 (s, 1 H), 7.4–7.6 (m, 2 H), 7.97 (s, 1 H), 7.7–8.0 (m, 2 H), 8.17 (s, 1 H); IR (KBr) 3360, 1684, 1437, 1398, 1034 cm^{-1}. Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 73.01; H, 7.36; N, 4.53.

Diastereomer B of 3-hydroxy-3-(2-methoxy-1,1,2-trimethylethyl)-2-methyl-1*H*-benz[*f*]isoindol-3(2*H*)-one (**32d**): mp 150–152 °C; ^{1}H NMR ($CDCl_3$) 0.54 (s, 3 H), 1.09 (d, 3 H), 1.25 (s, 3 H), 3.09 (s, 3 H), 3.40 (s, 3 H), 3.79 (q, 1 H), 5.74 (s, 1 H), 7.4–7.7 (m, 2 H), 7.75 (s, 1 H), 7.7–8.0 (m, 2 H), 8.16 (s, 1 H); IR (KBr) 3290, 1678, 1423, 1391, 1110, 790 cm^{-1}. Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.67; H, 7.53; N, 4.47.

Excitation and Emission Spectra of NMN. The corrected excitation spectrum of 1×10^{-4} M solution of NMN in acetonitrile was scanned from 200–400 nm at an emitting wavelength of 400 nm. Maxima were observed at 270, 308, 359, and 379 nm. The corrected emission spectrum was scanned from 320–520 nm at an excitation wavelength of 300 nm. Maxima were observed at 371 and 388 nm. The crossover wavelength of the excitation and emission spectra is 360.3 nm, which corresponds to a singlet state energy of 79 kcal/mol.

Reduction Potential of NMN. A cyclic voltammogram of NMN was measured by using a PAR 174A potentiostat equipped with a Houston 2000 Omnigraph XY recorder. The potential was measured by using a platinum square (0.5 cm) as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference. The solution contained 3×10^{-3} M NMN and 0.1 M tetraethylammonium perchlorate (TEAP) in acetonitrile (distilled over CaH_2). Scans of 20 mV/s were taken. A cyclic voltammogram of NMP take under these conditions gave a reduction potential of −1.40 V, as

compared to the literature value of -1.37 V. The reduction potential of NMN was measured as -1.65 V.

Fluorescence Quenching of NMN. General Conditions. Fluorescence quenching experiments were carried out on 1×10^{-4} M solutions of NMN in spectral grade acetonitrile. Typically, five samples containing from 10^{-3} to 10^{-2} M quencher were prepared. The excitation wavelength was 300 nm unless competitive absorption from the quencher was significant, in which case a longer excitation wavelength was chosen. Fluorescence intensities were monitored at 371 nm. The data was interpreted by using the standard Stern-Volmer relationship.

Fluorescence Quenching of NMN by 2,3-Butanedione. Estimation of the Singlet-State Lifetime of NMN. Efficient fluorescence quenching of NMN was observed in the presence of butanedione [(9.12×10^{-4})-(4.56×10^{-3}) M]. A Stern-Volmer plot of the data was linear with a slope of 101 ± 1. Since the singlet-state energy of butanedione is 65.3 kcal/mol and that of NMN is estimated to be 79 kcal/mol (vide supra) energy transfer should proceed at the diffusion-controlled rate, 2×10^{10} M/s in acetonitrile. The average $k_q\tau$ value for butanedione (and for 2,5-dimethyl-2,4-hexadiene) is 104 ± 3. The lifetime (τ) of the singlet state of NMN is calculated as 5.2 ns.

Solvent Isotope Studies. Identical samples containing 50 mg of NMP and 0.50 mL of **24** in 2 mL of the appropriate solvent (MeOH, MeOD, CH_3CN, CD_3CN) were irradiated through Pyrex in a merry-go-round apparatus. A minimum of three samples of each solvent was examined by HPLC vs. an internal standard. The **28**/**29** ratio was unchanged in MeOH/MeOD. The **28**/**29** ratio decreased by 16% in going from CH_3CN to CD_3CN.

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Polar Effects in Free-Radical Reactions. Rate Constants in Phenylation and New Methods of Selective Alkylation of Heteroaromatic Bases

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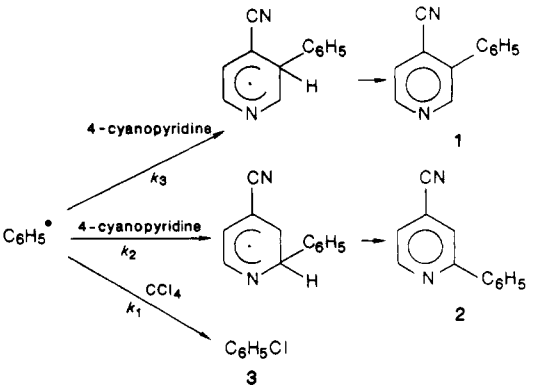
The rate constants for the addition of the phenyl radical to protonated and unprotonated 4-substituted pyridines have been determined by competition with chlorine abstraction from CCl_4. The constants range from 2×10^5 to 6×10^6 M^{-1} s^{-1} depending on the substituent and on the degree of protonation. The phenyl radical shows a clear-cut nucleophilic character. On the basis of these rate constants, the use of phenyl radical from diazonium salt or benzoyl peroxide to generate alkyl radicals by iodine or hydrogen abstraction has been developed as a general procedure for the alkylation of heteroaromatic bases. This reaction is characterized by high yields and selectivities.

The substitution of protonated heteroaromatic bases by nucleophilic carbon-centered radicals is a general reaction of large synthetic interest. It reproduces most of the numerous aspects of the Friedel-Crafts aromatic alkylation and acylation, but with opposite reactivity and selectivity.[1,2] Actually the high reactivity and selectivity and the consequent synthetic interest are not limited to the protonated heteroaromatic bases. They are quite general towards electron-deficient unsaturated compounds, particularly, if a positive charge is placed on the unsaturated system (pyrilium,[3] diazonium,[4] iminium salts[5]). This suggests a large contribution of charge separation to the transition states of these systems (eq 1). The homolytic

$$R^{\bullet} X{=}Y^{+} \leftrightarrow R^{+} X{=}Y^{\bullet} \qquad (1)$$

phenylation of heteroaromatic bases has been extensively investigated,[6] and the large change of selectivity by passing from unprotonated to protonated derivatives has been ascribed to the polar effect[7] rather than to the free valence numbers or the atom localization energies.[6] It was of interest to know the rate constants of the phenyl radical addition to protonated and unprotonated heteroaromatic bases mainly for two reasons: (i) a better understanding of the change of selectivity with the protonation and of the polar effect and (ii) the evaluation of the limits in utilizing the phenyl radical as source of more nucleophilic carbon-

Scheme I



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