washed with 1 N aqueous hydrochloric acid, 5% aqueous sodium bicarbonate solution, and water. The organic layer was dried (magnesium sulfate), the solvent was removed under reduced pressure, and the resulting brown oil was chromatographed on 60-200 mesh silica gel. The fraction eluted with 5:1 benzene:hexane was shown by GLC to contain the two major unknown products. Since the parent ions of neither compound could be detected with electron-impact GLC-MS conditions, chemical ionization (CI) GLC-MS was used with ethane ionizing gas. This method gave m/e 146 as the parent ion for both substances. In addition, a strong peak at m/e 118 was seen in each mass spectrum.

In an ESR spectroscopic study¹⁹ of this reaction, stable baselines were

obtained when separate solutions of the reactants in dioxolane solutions were scanned using a 9-GHz probe at -30 °C. However, mixing of the enolate solution with the solution of the nitro ester gave a mixture which immediately gave the deep red color and which exhibited a strong signal (triplet, splitting constant = 12 G), indicating the formation of radical species. Improved resolution of this spectrum gave evidence of overlapping peaks (Figure 2). However, the peaks could not be further resolved at -60°, at 25°, or by employing a 35-GHz probe at -100° to -35 °C.

(19) The authors would like to thank Dr. S. Balakrishnan for assistance in obtaining the ESR spectra.

Redox-Photosensitized Reactions. 7.¹ Aromatic Hydrocarbon-Photosensitized Electron-Transfer Reactions of Furan, Methylated Furans, 1,1-Diphenylethylene, and Indene with *p*-Dicyanobenzene

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Abstract: Electron-transfer reactions of furan, 2-methylfuran, 2,5-dimethylfuran, 1,1-diphenylethylene, and indene with p-dicyanobenzene are photosensitized by several selected aromatic hydrocarbons. With the furan compounds are formed the dihydrofurans having both the p-cyanophenyl and the methoxy groups by the phenanthrene-photosensitized reaction in 4:1 acetonitrile-methanol, whereas the photodimerization or anti-Markovnikov addition of alcohols occurs with the olefins. Kinetic studies on the anti-Markovnikov addition of methanol to 1,1-diphenylethylene suggest that the cation radical of phenanthrene forms a π complex with the olefin as a key intermediate. The mechanisms of the photosensitized reactions are discussed.

Recently, photoreactions involving electron-transfer events have received much attention from synthetic and mechanistic aspects of organic photochemistry² and also for chemical conversions of solar energy.³ In a variety of organic electron donor (D)-acceptor (A) pairs, photoexcitation of either A or D in polar media results in electron transfer from D to A, thus generating the cation radical of D and the anion radical of A.⁴ Numerous photoreactions of A-D pairs in polar solvents have been reported to proceed via the ion radicals, involving adduct formation between A and D,⁵ cyclodimerization of olefins,⁶ cross-addition between olefins,⁷ addition

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Scheme I



of nucleophiles to various substrates,⁸⁻¹⁰ methanolysis of alocohols and benzoates,¹¹ reductive removal of a protecting group,¹² bond-cleavage reactions,¹³ reduction of arenes¹⁴ and carbonyl

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Scheme II



compounds,² and oxidation of olefins;¹⁵ most of them are of potential synthetic utility.

In a previous communication,¹⁶ we reported that electrontransfer reactions of furan and a few olefins with p-dicyanobenzene (DCNB) are photosensitized by aromatic hydrocarbons (S) in polar media. We and others¹⁷ suggested that the photosensitized reactions proceed via initial electron transfer from the excited singlet state of S to DCNB and subsequent hole transfer from the cation radical of S to substrates (D). In other words, S can act as a mediator for electron transfer from D to DCNB (A) upon photoexcitation in a manner similar to photochemical electrontransfer mediation by Ru(II) complexes¹⁸ and by chlorophyll molecules in reaction center of photosynthesis.¹⁹ This type of photosensitization, which we call "redox photosensitization", is completely different from photosensitization involving energy transfer and should also be discriminated from "electron-transfer photosensitization" that has been reported mainly by Arnold^{8,13} and Farid.^{6c,7a,15d} Redox photosensitization can be delineated as in Scheme I.

Moreover, we assumed that a key mechanistic pathway is the π -complex formation between the cation radical of S (S⁺) and D in cases where the oxidation potential of S is lower than that of D. The π -complex mechanism has been strongly suggested for redox-photosensitized cycloreversion of cyclobutane compounds.^{1,20} However, an alternative interpretation could be made by assuming that D^+ is formed as the reactive species in equilibrium of eq 1.

$$S^+ \cdot + D \rightleftharpoons S + D^+ \cdot \rightarrow \text{products}$$
 (1)

In order to establish the mechanism, therefore, we have carried out extensive kinetic studies on the phenanthrene-photosensitized anti-Markovnikov addition of methanol to 1,1-diphenylethylene, a typical reaction system in which the oxidation potential of the olefin is higher than that of phenanthrene. Moreover, product distributions in the redox-photosensitized reactions of some furan and olefinic compounds have been investigated in detail with regard to synthetic potentiality of the redox photosensitization.

Results

Redox-Photosensitized Reactions of Furan, 2-Methylfuran, and 2.5-Dimethylfuran. Irradiation of a 4:1 acetonitrile-methanol

Scheme III



solution containing phenanthrene (P), furan (F), and p-dicyanobenzene (DCNB) in a Pyrex vessel with a high-pressure mercury lamp gave 1 in 74% isolated yield based on unrecovered DCNB. Control runs revealed that 1 was formed in >90% yield (GLC) without any change in the amount of P and that irradiation at 313 nm in the absence of P did not give 1. Similarly, the photosensitized reactions of 2-methylfuran (MF) and 2,5-dimethylfuran (DF) gave 2-5. In all the runs, P was recovered in 76-90%. The results are summarized in Scheme II.

NMR analyses showed that 1, 3, or 5 is a single isomer each, whereas 2 and 4 are 1:1 mixture of the cis and trans isomers, respectively. The structures of the products were strongly indicated by their spectral properties and firmly established by chemical transformations shown in Scheme III, though the configuration of 1, 3, and 5 has not been determined.

Redox-Photosensitized Reactions of 1,1-Diphenylethylene. As shown in Scheme IV, irradiation of an acetonitrile solution containing P, 1,1-diphenylethylene (DPE), and DCNB gave 6 in 89% yield, whereas the photoreaction in 4:1 acetonitrile-methanol afforded 7 and 8. It was confirmed that the formation of 7 at 313 nm in the absence of P is only less than one-tenth as efficient as that in the presence of 0.01 M P.

Redox-Photosensitized Reactions of Indene. Irradiation of an acetonitrile solution containing P, indene (IN), and DCNB gave the cis.syn- and trans,syn-cyclobutane dimers of IN in a 5:95 ratio at low conversion (<10%) while the anti dimers could not be detected. In 4:1 acetonitrile-water, 2-indanol (9) was mainly formed along with 10, 11, and 12. Similarly, the photoreaction

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Redox-Photosensitized Reactions

Table I. Quantum Yields for Aromatic Hydrocarbon-Photosensitized Reactions of Furan, 1,1-Diphenylethylene, and Indene with $DCNB^{\alpha}$ and Oxidation Potentials

S	$E_{p_{/2}}^{ox}$, V	$\phi_1^{\ b}$ F 1.40	φ ₇ ^c DPE 1.32	φ ₁₃ ^d IN 1.17
triphenylene	1.29	0.21	0.41	0.33
naphthalene	1.22	0.15	0.38	0.30
phenanthrene (P)	1.17	0.10	0.36	0.25
1,4-dimethylnaphthalene	1.10	ND^e	0.25	ND^{e}
chrysene	1.05	0.05	0.14	0.19
1,3-dimethylnaphthalene	1.02	ND^{e}	0.13	ND ^e
2, 3-dimethy Inaphthalene	0.99	ND^{e}	0.11	ND^{e}
pyrene	0.78	0.00	0.00	0.00
anthracene	0.75	0.00	0.00	0.00

 a Degassed 4:1 acetonitrile-methanol solution; [S] = 0.01 M and [DCNB] = 0.1 M; at 313 nm. b Quantum yields for the 1 formation at 1.0 M F. c Quantum yields for the 7 formation at 0.1 M DPE. d Quantum yields for the 13 formation at 0.1 M IN. e Photosensitized reactions occurred but quantum yields were not determined.



Figure 1. Least-squares plots of ϕ_7^{-1} vs. $[DPE]^{-1}$ for the phenanthrenephotosensitized addition of methanol to DPE at 313 nm; (O) 6.1×10^{-8} einstein/min; (\bullet) 2.3 × 10⁻⁸ einstein/min. The slope and intercept are 1.8 × 10⁻² M and 2.8, respectively. See footnotes in Table II.

in 4:1 acetonitrile-methanol gave 13, 14, and 15. The photosensitized anti-Markovnikov addition of other alcohols to IN was attempted, and the adducts were isolated in moderate yields. The results are shown in Scheme V; yields are based on IN unrecovered.²¹

Compound 15 was obtained as a diastereoisomeric mixture, whereas 11, 12, and 14 were isolated as crystalline materials. The structure determination of 9, 12, 13, and 15 was carried out by direct comparison with authentic samples.^{5b} The structures of 11 and 14 were indicated by elemental composition data and spectral properties. Since 10 did not solidify, it was converted to the keto ester 21 by chromic acid oxidation followed by esterification of the resulting keto acid with diazomethane.



A direct photoreaction of IN with DCNB in 4:1 acetonitrilemethanol in the absence of P was attempted for comparison with the phenanthrene-photosensitized reaction. Although the direct photoreaction gave again 13, 14, and 15, it should be noted that longer irradiation time was required and considerable amounts of oligomeric compounds were formed. Thus, yields of 13 and 14 were 30% (based on unrecovered IN) and 6.3% (40% based on unrecovered DCNB), respectively, much lower than those in the phenanthrene-photosensitized reaction.

Redox-Photosensitized Reactions with Other Aromatic Hydrocarbons. The photosensitized reactions described above were

Table II. Dependence of Quantum Yields (ϕ_{γ}) on Concentration of DPE and Light Intensity for the Phenanthrene-Photosensitized Anti-Markovnikov Addition of Methanol of DPE^{*a*}

light				10 ³ [DI	PE], M			
intensity ^b	11.4	12.8	14.5	16.0	20.0	40.0	76.0	c
6.1 × 10 ⁻⁸	0.238		0.244		0.286	0.328	0.318	0.260
2.3×10^{-8}		0.256		0.246		0.294	0.370	0.360

^a Degassed 4:1 acetonitrile-methanol solution; [P] = 0.01 M and [DCNB] = 0.1 M; at 313 nm. ^b Einstein/min. ^c Extrapolated value (ϕ_{σ}^{∞}) ; see Figure 1.



Figure 2. Least-squares plot of ϕ_7^{-1} vs. [MeOH]⁻¹ for the phenanthrene-photosensitized addition of methanol to DPE at 313 nm; [P] = 0.01 M, [DPE] = 0.1 M, and [DCNB] = 0.1 M. The slope and intercept are 3.5 M and 2.5, respectively.



Figure 3. Least-squares plot of $\phi_7/\phi_7^{\rm Q}$ vs. [TEA] at [TEA] $< 2 \times 10^{-3}$ M for quenching of the phenanthrene-photosensitized addition of methanol to DPE by TEA. See footnote *a* in Table III.

effected by the other aromatic hydrocarbons involving triphenylene (TR), naphthalene (NT), chrysene (CR), and the three dimethylnaphthalenes, while pyrene and anthracene were not effective. It was again confirmed by GLC that the effective arenes are not consumed after the completion of the photoreactions. Quantum yields for the formation of 1, 7, and 13 were determined at 313 nm. Table I lists the quantum yields together with the oxidation potentials of S and D that are the anodic half-peak potentials in the irreversible cyclic voltammograms in acetonitrile.²²

Kinetic Results for Redox-Photosensitized Anti-Markovnikov Addition of Methanol to DPE. A. Quantum Yields. Detailed kinetic measurements were carried out for the anti-Markovnikov addition of methanol to DPE by the redox photosensitization at 313 nm, using P (0.01 M) and DCNB (0.1 M) in 4:1 acetonitrile-methanol. The formation of 7 at 0.1 M in DPE increased linearly with irradiation time up to ~9% conversion, where the formation of 8 was negligibly small. Therefore, quantum yields for the 7 formation (ϕ_7) were determined at less than 6% conversion. A plot of ϕ_7^{-1} vs. the reciprocal of [DPE] is linear and independent of the intensity of the incident light at 313 nm (Figure 1 and Table II). It was found that ϕ_7 depends on concentration of methanol as well (Figure 2) but not on concentration of P.

⁽²¹⁾ Yields of 10, 11, and 14 are 32%, 40%, and 80%, respectively, based on DCNB unrecovered.

⁽²²⁾ Unless otherwise specified, $E_{p/2}^{\alpha x}$'s are the irreversible half-peak potentials vs. Ag/Ag⁺ in acetonitrile.

Table III. Slopes in the Linear Region of Stern-Volmer Plots in the Quenching of Phenanthrene-Photosensitized Addition of Methanol to DPE by Various Quenchers^a

quencher	$E_{p/2}^{ox}(Q),$	$\begin{array}{c} K_{SV},^{b} \\ V & M^{-1} \end{array}$
anisole	1.30	0.12
o-methylanisole	1.20 ^c	470
hexamethylbenzene	1.16	165
<i>p</i> -methylanisole	1.11 ^c	275
1,3,5-trimethoxybenzene	1.01	2200
o-dimethoxybenzene	0.97 ^c	3000
<i>p</i> -dimethoxybenzene (DMB)	0.90 ^c	2900
triethylamine (TEA)	0.37	2420

^a Degassed 4:1 acetonitrile-methanol solution; [P] = 0.01 M, [DPE] = 0.1 M, and [DCNB] = 0.1 M; at 313 nm. ^b Slopes of the linear Stern-Volmer plots at lower concentrations of the quenchers; for example, see Figure 3. ^c Reversible half-wave oxidation potentials.



Figure 4. Least-squares plot of ϕ_7/ϕ_1^Q vs. [TEA] at [TEA] > 2 × 10⁻³ M for quenching of the phenanthrene-photosensitized addition of methanol to DPE by TEA. See footnote *a* in Table III.



Figure 5. Least-squares plot of $\phi_7/\phi_7^{\rm Q}$ vs. [DPE]⁻¹ in the presence of 1 $\times 10^{-3}$ M TEA for the phenanthrene-photosensitized addition of methanol to DPE. The slope and intercept are 2.95 $\times 10^{-3}$ M and 3.31 respectively. See footnote *a* in Table II.

B. Quenching by Cation-Radical Quenchers. The photosensitized reaction was quenched by triethylamine (TEA) and other compounds of low oxidation potentials. The Stern-Volmer plots are linear at lower concentrations of the quenchers ($< 2 \times 10^{-3}$ M); Figure 3 shows a typical plot for the quenching by TEA. Table III lists the slopes (K_{SV}) of the linear Stern-Volmer plots together with the oxidation potentials of the quenchers. Figure 5 shows the dependence of ϕ_7/ϕ_7^Q on concentration of DPE in the presence of 10^{-3} M TEA.

At higher concentrations of TEA, however, the Stern-Volmer plot deviates upward from linearity at lower concentrations (Figure 4). The curvature would be caused by either the formation of CT complexes in the ground state or competitive quenching of excited singlet P by TEA. UV measurements revealed that no CT complexes are formed between TEA and P or DCNB, even at the maximum concentration $(1.5 \times 10^{-2} \text{ M})$ of TEA used in the quenching experiment. The rate constant for quenching of the P fluorescence by TEA was determined to be $7 \times 10^8 \text{ M}^{-1}$ s⁻¹ in 4:1 acetonitrile-methanol, which is much smaller than that



Figure 6. Least-squares plot of ϕ_7/ϕ_7^Q vs. [DMB] for quenching of the phenanthrene-photosensitized addition of methanol to DPE by DMB. See footnote *a* in Table III.

 Table IV.
 Rate Constants for Fluorescence Quenching by DCNB

 and Calculated Free-Energy Changes

fluorophor (S)	$\tau_{\rm F}$, ^{<i>a</i>, <i>b</i>} ns	$10^{-10}k_{q}F, a, c$ M ⁻¹ s ⁻¹	$E_{0-0}({}^{1}S^{*}), d$ kcal/mol	$\Delta G,^e$ kcal/mol
triphenylene	34 ± 0.5^{f}	1.4^{f}	83.4	-9.1
naphthalene	118 ^{g, h}	1.2^{g}	92	-21.1
phenanthrene	60 ± 1^{g} 17 ± 1 ^f	2.0^{g} 1.5^{f}	82.9	-13.2
chrysene	48 ± 0.5^{f}	1.2^{f}	79.2	12.2

^a Degassed solution; $[S] = 10^{-3} \sim 10^{-4}$ M. ^b Fluorescence lifetimes. ^c Fluorescence-quenching rate constants. ^d Excited singlet energies of S abstracted from Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973. ^e Calculated free-energy changes in acetonitrile using eq 3; $E_{p,2}$ ^{red}(DCNB) = -1.91 V vs. Ag/Ag⁺ in acetonitrile; the coulombic term (e^2/ea) is estimated to be 1.3 kcal/mol. ^f In 3:1 acetonitrile-methanol. ^g In acetonitrile. ^h Mataga, N.; Tamura, M.; Nishimura, H. Mol. Phys. 1965, 9, 367.

Table V. Rate Constants for Phenanthrene-Photosensitized Anti-Markovnikov Addition of Methanol to DPE^a

process	symbol	value
formation of C ⁺ . nucleophilic attack of methanol on C ⁺ .	k _c k _M c	$3.4 \times 10^{9} \text{ M}^{-1} \text{ s}^{-1}$ 7.0 × 10 ⁵ M ⁻¹ s ⁻¹
decay of P^+ . decay of C^+ .	$k_X[X] \\ k_X^c[X]$	$2.2 \times 10^{7} \text{ s}^{-1}$ $9.8 \times 10^{5} \text{ s}^{-1}$
limiting quantum yield for 7 formation	αβ	0.53

^a In 4:1 acetonitrile-methanol; see text

by DCNB $(1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$. Thus, the quenching of excited singlet P by 1.5×10^{-2} M TEA is calculated to correspond with less than 1% that by 0.1 M DCNB. Therefore, it is safely concluded that the curved Stern-Volmer plot arises from quenching of cation radical intermediates.

In contrast, the Stern-Volmer plot for quenching by p-dimethoxybenzene (DMB) deviates downward with an increase of concentration of DMB from linearity at lower concentrations and then reaches a new linear line of a lower slope as shown in Figure 6.

Discussion

Primary Process. The fluorescence of the aromatic hydrocarbons (S) was quenched by DCNB at the diffusion-controlled limits in acetonitrile and 4:1 acetonitrile-methanol (Table IV) but not by the substrates (D) to significant extents. The photosensitized reactions in 4:1 acetonitrile-methanol shown in Schemes II, IV, and V were neither quenched by 1.0 M isoprene, a triplet quencher, nor sensitized by benzophenone and acetophenone, whose triplet energies are higher than that of P. Therefore, it is concluded that a singlet mechanism is responsible for the photosensitized reactions.

Table IV lists the excitation energies of S $[E_{\infty,\infty}(^{1}S^{*})]$, the observed rate constants (k_{q}^{F}) for quenching of the S fluorescence

Scheme V



by DCNB, and the free-energy changes (ΔG) associated with electron transfer from excited singlet S to DCNB (eq 2). The

$$^{1}S^{*} + DCNB \rightarrow S^{+} + DCNB^{-}$$
 (2)

$$\Delta G = 23.06 \left[E_{p/2}^{\text{ox}}(S) - E_{p/2}^{\text{red}}(DCNB) - e^2/\epsilon a \right] - E_{0.0}(^{1}S^{*})$$
(3)

 ΔG values which are calculated according to eq 3²³ are substantially negative, thus indicating that electron transfer of eq 2 occurs at the diffusion-controlled rates. In fact, it was reported that the cation radicals of pyrene²⁴ and phenanthrene^{17a} are detected by means of laser flash photolyses of the pyrene– and phenanthrene–DCNB–acetonitrile systems.

Follow-up Processes. The formation of all products can be explained by assuming the intervention of the cation radical of the substrates. For example, the observed isomer ratio of the trans, syn and cis, syn dimers of IN is identical with that reported for the dimerization via the cation radical of IN.^{6c} Moreover, the formation of the tetralin dimer of DPE (6) and the methanol adduct (7) in the photoreaction of DPE with methyl *p*-cyanobenzoate has been established to occur via the cation radical of DPE.^{8a}

Scheme VI delineates the possible follow-up processes; the cation radicals of substrates (D^+) or π complexes $[(S \cdot D)^{+}]$ (vide infra) react with nucleophiles (ROH) to give adduct radicals $(\cdot D - OR)$ or with D to generate dimer cation radicals (D_2^+) . The latter species receive electrons from DCNB⁻ and/or D to give the dimers⁶ or react with ROH to generate $\cdot D_2$ -OR. The water and alcohol adducts are thus formed by one-electron reduction of $\cdot D_n$ -OR (n = 1 and 2) with DCNB⁻, whereas a radical-coupling reaction between $\cdot D_n$ -OR and DCNB⁻ affords the cyanophenylated compounds.

Hole-Transfer Process. As shown in Table I, quantum yields for the product formation are relatively high even in cases where $E_{p/2}^{ox}(S) \le E_{p/2}^{ox}(D)$; for example, see the columns for F and DPE in Table I. In these cases, complete hole transfer from S⁺ to D is probably endothermic. Therefore, this process is unlikely to play important roles in the efficient photoreactions. Therefore, we previously assumed the intervention of π complexes formed

Scheme VI

 $S^{+} + D \longrightarrow (S^{+}D)^{+} \text{ or } S + D^{+}$ (4)

$$S \cdot D)^+ \cdot or D^+ \cdot + ROH \longrightarrow \cdot D - OR + H^+ (+ S)$$
 (5)

$$S^{+}D)^{+} \circ D^{+} + D \longrightarrow D_{2}^{+} (+ S)$$
 (6)

$$D_2^+ + ROH \longrightarrow D_2^-OR + H^+$$
 (7)

$$D_2^+ \cdot + DCNB^- \cdot and/or D \longrightarrow D_2 + DCNB and/or D^+ \cdot (8)$$

$$D_n - OR + DCNB^{-} + DCNB^{-} + D_n - OR + D_n - OR$$

NC (-)
$$D_{\rho}$$
 OR $-CN^{-}$ Ar- D_{ρ} OR (10)
 $n = 1; 1-5, 10, 14$
 $n = 2; 11$



between S⁺ and D (Scheme I);¹⁶ nucleophiles or neutral molecules of D attack the D side of π complexes, where a partial positive charge develops. The π -complex mechanism has been strongly indicated for redox-photosensitized cycloreversions of some cyclobutane compounds^{1,20} and is further supported by kinetic analyses for the phenanthrene-photosensitized anti-Markovnikov addition of methanol to DPE.

On the other hand, S⁺ can rapidly abstract an electron from D (eq 12) in cases where $E_{p/2}^{ox}(S) > E_{p/2}^{ox}(D)$ since this process is certainly exothermic. This would fit the cases where D = MF ($E_{p/2}^{ox} = 1.14$ V), DF (0.93 V), or IN and S = TR or NT, though no efforts were made to clarify the mechanism.

$$S^+ \cdot + D \to S + D^+ \cdot \tag{12}$$

⁽²³⁾ Rehm, D.; Weller, A. Isr. J. Chem. 1970, 8, 259.

⁽²⁴⁾ Hino, T.; Masuhara, H.; Mataga, N. Bull. Chem. Soc. Jpn. 1976, 49, 394.

S

. . .

Scheme VII^a

$$S \xrightarrow{h\nu} S^*$$
(13)
$$IS^* = \frac{1/\tau_F}{1} S^*$$
(14)

$$^{1}S^{*} \xrightarrow{\Delta H_{P}} S \qquad (14)$$

$$^{1}S^{*} + DCNB \xrightarrow{\alpha k_{Q}} F S^{*} + DCNB^{-} (15)$$

$$^{4}S^{*} + DCNB \xrightarrow{(1-\alpha)k_{q}F} S + DCNB$$
 (16)

$$S^{+} + D \xrightarrow{k_c} (S \cdot D)^{+} \equiv C^{+} \cdot$$
 (17)

$$+ X \xrightarrow{k_X} S$$
 and/or others (18)

$$S^{\bullet} + Q \xrightarrow{\sim} S + Q^{\bullet}$$
(19)

$$C^{+} + \text{MeOH} \xrightarrow{h \to \infty} S + D - OMe + H^{+}$$
(20)

$$C^{+} + D \xrightarrow{\sim} S + D_{2}^{+}$$
(21)

$$C^* + X \xrightarrow{RX} S + D \text{ and/or others}$$
 (22)

$$C^{+} + Q \xrightarrow{\kappa_Q} S + Q^{+}$$
(23)

$$D-OMe \xrightarrow{P} 7 (24)$$

$$D_2^+ + MeOH \xrightarrow{} DCNB^-$$
 (25)

$$Q^+ + X \rightarrow Q$$
 and/or others (26)

^a S = phenanthrene, D = 1,1-diphenylethylene, Q = triethylamine, and X = impurities.

Analyses of Kinetics for the Redox-Photosensitized Anti-Markovnikov Addition of Methanol to DPE. On the basis of the above discussions, the possible mechanistic pathways are shown in Scheme VII. The cation radical species, S^+ and $(S^-D)^+$, may lose the positive charge by charge neutralization with DCNB⁻ or may be deactivated by impurities. However, the former process can be considered to be not important since ϕ_7 does not depend on the light intensity. Formation of the dimer cation radical of S (S₂⁺), which would be another deactivation process, can be safely neglected since ϕ_7 is independent of concentration of P. Since the fluorescence of P is completely quenched by 0.1 M DCNB, unimolecular processes from ¹S^{*} can be also neglected in kinetic analyses.

In the absence of Q, steady-state analysis gives eq 27, where

$$\frac{1}{\phi_7} = \frac{1}{\alpha\beta} \left(1 + \frac{k_{\rm X}^{\rm c}[{\rm X}]}{k_{\rm M}^{\rm c}[{\rm MeOH}]} \right) \left(1 + \frac{k_{\rm X}[{\rm X}]}{k_{\rm c}[{\rm D}]} \right) \quad (27)$$

 α and β represent the limiting quantum yield for the S⁺ formation and the fraction of the 7 formation from \cdot D–OMe, respectively. In this equation, it has been assumed that $k_{\rm X}^{\rm c}[{\rm X}] \gg k_{\rm D}^{\rm c}[{\rm D}]$ since a plot of ϕ_7^{-1} vs. the reciprocal of [D] is linear. From the intercept-to-slope ratios of Figures 1 and 2, the rate ratios in eq 28 and 29 are obtained. The $\alpha\beta$ value can thus be calculated from eq 28 and the intercept of Figure 1 to be 0.53 or from eq 29 and the intercept of Figure 2 to be 0.43. Although these values are close to each other, the former was employed for the value in 4:1 acetonitrile–methanol since the latter is an extrapolated value from lower concentrations of methanol.

$$k_{\rm X}[{\rm X}]/k_{\rm c} = 6.4 \times 10^{-3} \,{\rm M}$$
 (28)

$$k_{\rm X}^{\rm c}[{\rm X}]/k_{\rm M}^{\rm c} = 1.4$$
 (29)

$$\alpha\beta = 0.53 \tag{30}$$

In the presence of Q (TEA), the Stern-Volmer equation can be represented by eq 31, where it has been assumed from eq 28

$$\frac{\phi_7}{\phi_7^{\rm Q}} = \left(1 + \frac{k_{\rm Q}^{\rm c}[{\rm Q}]}{k_{\rm M}^{\rm c}[{\rm MeOH}] + k_{\rm X}^{\rm c}[{\rm X}]}\right) \left(1 + \frac{k_{\rm Q}[{\rm Q}]}{k_{\rm c}[{\rm D}]}\right) \quad (31)$$

that $k_c[D] \gg k_X[X]$. The quadratic Stern-Volmer plot in Figure



Figure 7. Plot of log K_{SV} vs. $[E_{p/2}^{ox}(Q) - E_{p/2}^{ox}(P)]$ for quenching of the phenanthrene-photosensitized addition of methanol to DPE by various quenchers. See footnotes in Table III.

4 is in good accord with eq 31. At lower concentrations of Q, eq 31 can be reduced to eq 32, which is then rewritten as eq 33 for analysis of the plot in Figure 5.

$$\frac{\phi_7}{\phi_7^{\rm Q}} = 1 + \left(\frac{k_{\rm Q}^{\rm c}}{k_{\rm M}^{\rm c}[{\rm MeOH}] + k_{\rm X}^{\rm c}[{\rm X}]} + \frac{k_{\rm Q}[{\rm Q}]}{k_{\rm c}[{\rm D}]}\right) [{\rm Q}] \qquad (32)$$

$$= \left(1 + \frac{k_{\mathrm{Q}}^{\mathrm{c}}[\mathrm{Q}]}{k_{\mathrm{M}}^{\mathrm{c}}[\mathrm{MeOH}] + k_{\mathrm{X}}^{\mathrm{c}}[\mathrm{X}]}\right) + \frac{k_{\mathrm{Q}}[\mathrm{Q}]}{k_{\mathrm{c}}[\mathrm{D}]} \quad (33)$$

From the slope of the plot in Figure 5, the value of k_Q/k_c is determined to be 2.95. The value of k_Q^c/k_M^c is also calculated to be 1.5×10^4 , using both the intercept of the plot in Figure 5 and eq 29. Since k_Q^c/k_M^c [MeOH] $\gg k_Q/k_c$ [D], it is evident that the linear Stern-Volmer plot at lower concentrations of Q exclusively originates from quenching of C⁺. Therefore, the slope of the Stern-Volmer plot at lower concentrations of Q (K_{SV}) can be approximately represented by eq 34; from the slope (K_{SV}) of

$$K_{\rm SV} = \frac{k_{\rm Q}^{\rm c}}{k_{\rm M}^{\rm c}[{\rm MeOH}] + k_{\rm X}^{\rm c}[{\rm X}]}$$
(34)

Figure 3 and eq 29, the value of k_Q^c/k_M^c can be separately calculated to be 1.6×10^4 , being in good accord with that obtained from the intercept of Figure 5.

Equation 34 appears to hold for quenching by the other quenchers of low oxidation potentials as well. Therefore, the K_{SV} values reflect the rate constants for quenching of C⁺. by the quenchers. As shown in Figure 7, the logarithmic values of K_{SV} reach an almost constant value when the oxidation potentials of the quenchers are more than 0.16 V as low as that of P, thus demonstrating that the quenching of C⁺. by TEA occurs at the diffusion-controlled limit, i.e., $k_Q^c = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Moreover, it is reasonable to assume that $k_Q^c = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ since the quenching process is exothermic by 18.4 kcal/mol (0.80 V). All the rate constants can thus be calculated and are listed in Table V.

Discussion of Kinetic Results. Since the k_c value is close to the diffusion-controlled rate constant, an interaction between DPE and the cation radical of P (P⁺·) appears to be a slightly exothermic process. However, the complete hole-transfer process (eq 12) involving formation of the discrete cation radical of DPE might be endothermic by 3.5 kcal/mol judging from the oxidation potentials of P and DPE. Under the assumption that irreversible anodic half-peak potentials can be used for a linear free-energy relationship in the one-electron oxidation process of similar compounds,²⁵ the net rate constant $(k_{\rm ht})$ of eq 12 can be estimated according to the Rehm-Weller's treatment²³ by using eq 35, 36, and 37. In eq 36, it has been assumed that $(k_M^{c}[MeOH] +$ $k_{X}^{c}[X] \gg k_{12}[S]$; this assumption leads to the maximum value of $k_{\rm ht}$. Thus the $k_{\rm ht}$ value is calculated to be 2.5 \times 10⁷ M⁻¹ s⁻¹, using the following set of parameters: $k_{12} = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $\Delta V k_{23}^{0} = 8 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, T = 293 K, $\Delta G^{+}(0) = 2.5 \text{ kcal/mol}$, and $\Delta G = 3.5$ kcal/mol. Although this value is not accurate,^{25a}

$$k_{\text{hr}} = \frac{k_{12}}{1 + \frac{k_{21}}{k_{23}}(1 + \frac{k_{32}}{k_{21}})} = \frac{k_{12}}{1 + \frac{k_{12}}{\Delta V k_{23}0}} (36)$$

$$\Delta G^{\#} = \frac{\Delta G}{2} + \left[\left(\frac{\Delta G}{2}\right)^{2} + \left(\Delta G(0)\right)^{2}\right]^{1/2} (37)$$

it is noteable that the calculated value is smaller by 2 orders of magnitude than the observed value of k_c . Therefore, the hole-transfer mechanism is unlikely to be accepted.

On the other hand, the large value of k_c can be reasonably interpreted by the π -complex mechanism; formation of C⁺ appears to be exothermic by stabilization arising from charge resonance as has been reported for the dimer cation radical of pyrene in solution²⁶ and π -complex cation radicals between different methylated benzenes in the vapor phase.²⁷ Furthermore, it should be noted that the k_M^c value is much smaller than the reported rate constant for the reaction of the free cation radical of DPE with ethanol ($1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in dichloromethane).²⁸ This is again in line with the π -complex mechanism since a π complex is certainly a weaker electrophile than the discrete cation radical of DPE owing to less development of the positive charge on the side of DPE in the π complex.

As shown in Figure 8, ϕ_7 at 0.1 M DPE decreases with a decrease of $E_{p/2}^{ox}(S)$, perhaps suggesting that charge resonance is important in binding of π complexes. Although ϕ_7 includes a variety of rate constants, its dependence on $E_{p/2}^{ox}(S)$ probably reflects changes of k_c/k_x and k_M^c/k_X^c ; α is known to be almost constant for similar electron donor-acceptor pairs in cases where ΔG of eq 3 is negative.²⁹ In the case of P, it has been demonstrated in the preceding section that $k_c[D] \gg k_x[X]$ at 0.1 M DPE. This might be true in cases where $E_{p/2}^{ox}(S) \ge 1.17$ V. Therefore, it is evident that k_M^c/k_X^c increases with an increase of $E_{p/2}^{ox}(S)$, probably reaching the value for the discrete cation radical of DPE; the higher the oxidation potential of S, the faster the nucleophilic attack of methanol on the π complex. On the other hand, a decrease of $E_{p/2}^{ox}(S)$ at <1.05 V may lead to decreases of both k_c/k_X and k_M^c/k_X^c ; there is the lowest limit of $E_{p/2}^{ox}(S)$ around 0.9 V for the occurrence of the photosensitized reaction.

Finally, the Stern-Volmer plot for quenching by DMB should be discussed. At lower concentrations, the linear line of a greater slope clearly originates from diffusion-controlled quenching of both C⁺ and P⁺ by DMB as has already been discussed. At ≥ 0.01 M DMB, however, the quenching is extremely slowed down. In other words, the nucleophilic addition of methanol to DPE still proceeds by means of an unquencherable mechanism under the conditions where both C⁺ and P⁺ have been mostly scavenged. This is in sharp contrast to quenching by TEA, in which no unquencherable mechanism participates. Therefore, it appears that the cation radical of DMB can catalyze the addition of methanol to DPE unlike the cation radical of TEA. The oxidation potential of DMB (0.90 V) is probably too low for complete hole

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(b) Rodgers, M. A. J. Chem. Phys. Lett. 1971, 9, 107.
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(27) Neot-Ner, M.; Hunter, E. P.; Field, F. H. J. Am. Chem. Soc. 1978, 100, 5466.



Figure 8. Plot of ϕ_7 vs. $E_{p/2}^{ox}(S)$ for the aromatic hydrocarbon-photosensitized addition of methanol to DPE; see Table I. The solid circle (\bullet) is the value for DMB obtained from the intercept of the linear line at higher concentrations of DMB in Figure 6.

Scheme VIII^a

C^{*} and S^{*} + DMB → S + D and S + DMB^{*}. DMB^{*} + D → (DMB·D)^{*}. DMB^{*} + DMB → (DMB)₂^{*}. DMB^{*} + X → DMB and/or others (DMB·D)^{*} + MeOH $\xrightarrow{\text{DCNB}^-}$. DMB + 7 (DMB·D)^{*} + X → DMB + D and/or others

^{*a*} DMB = p-dimethoxybenzene.

transfer from DMB⁺ to DPE to occur. Scheme VIII shows the reaction pathways at higher concentrations of DMB; competitive formation of the dimer cation radical of DMB is taken into consideration as an additional deactivation pathway since the π -complex formation between DMB⁺ and DPE is probably slow.

Synthetic Potentiality of Redox Photosensitization. Chemical yields as well as quantum efficiencies are moderate or high in the redox-photosensitized reactions as shown in Schemes II, IV, and V and in Table I. The redox photosensitization enables the anti-Markovnikov addition of various alcohols to IN to occur in moderate yields. In particular, it is notable that the phenan-threne-photosensitized addition of methanol to IN took place more cleanly and efficiently than the direct photoreaction. Similarly, chemical yield of the addition of methanol to DPE was remarkably improved by the photosensitization using phenanthrene compared with the direct photoreaction.^{8a} The redox photosensitization will be thus successfully applicable to the anti-Markovnikov addition of such weak nucleophiles as water and alcohols to DPE, IN, and related olefins.⁸ The synthetic feasibilities are further indicated by the fact that the direct photoreaction of DCNB with furan at >250 nm gave complex mixtures.

In direct photoreactions of electron donor-acceptor pairs, there must be involved the excited state(s) of A or D, exciplexes, and/or ion radical pairs, all of which may undergo other reactions competitively with formation of the free ion radicals, thus exerting unfavorable effects on pertinent reactions. On the other hand, the excited singlet and triplet arenes are usually stable toward unimolecular chemical changes and may give chemically inactive exciplexes and ion radical pairs with DCNB. In fact, no appreciable consumption of both P and DCNB was observed after prolonged irradiation of a 4:1 acetonitrile-methanol solution in either the presence or the absence of D. A benefit to its synthetic potentiality may be also given by the chemical inertness of S^+ . toward such weak nucleophiles as water, alcohols, and π bases. However, since S⁺ efficiently reacts with cyanide anion to give cvanated compounds, 10a,b the redox photosensitization can not be used for the photocyanation of olefins.^{8b}.

Conclusions

The redox photosensitization using the aromatic hydrocarbon-DCNB pairs in acetonitrile or 4:1 acetonitrile-methanol causes the reactions from the cation radicals of the furan and

^{(25) (}a) Klinger and Kochi^{25b} revealed evidence corroborating a linear free-energy relationship in the totally irreversible anodic oxidation of various homoleptic alkylmetals on the basis of a linear correlation of the anodic peak potentials with their ionization potentials in the gas phase. It is also known that the oxidation potentials of various arenes are linearly correlated with the ionization potentials.^{25c} However, the estimation of ΔG in one-electron tranfer processes is not very accurate when irreversible half-peak potentials are used. (b) Klinger, R. J.; Kochi, J. K. J. Am. Chem. Soc. 1980, 102, 4790; (c) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. J. Org. Chem. 1972, 37, 916. (26) (a) Kira, A.; Arai, S.; Imamura, M. J. Chem. Phys. 1971, 54, 4890;

⁽²⁸⁾ Hayashi, K.; Irie, M.; Lindnau, D.; Schnabel, W. Rad. Phys. Chem. 1978, 11, 139.

⁽²⁹⁾ Hino, T.; Akazawa, H.; Mashuhara, H.; Mataga, N. J. Phys. Chem. 1976, 80, 33.

olefinic compounds and will be also applicable to other similar substrates that are electron donors. It is strongly suggested that a key mechanistic pathway is the π -complex formation between S⁺ and D in cases where $E_{p/2}^{ox}(S) < E_{p/2}^{ox}(D)$; the π complexes are stabilized by charge resonance. Nucleophiles or neutral molecules of D react only with the D side of π complex where a partial positive charge develops. In other words, the π complexes are chemically equivalent to the discrete cation radicals of the substrates. In cases where $E_{p/2}^{ox}(S) > E_{p/2}^{ox}(D)$, complete hole transfer from S⁺ to D can occur to generate the discrete cation radical of D as a product-forming intermediate. We are now intending to carry out further mechanistic investigations using a laser-flash photolysis method.

At any rate, an essential point of redox photosensitization is that S^+ can activate electron-donating substrates though it is chemically stable toward such weak nucleophiles as water, alcohols, and π bases. In short, the photogenerated cation radical of aromatic hydrocarbons is a catalyst to cause a variety of reactions involving the addition of nucleophiles to furan and olefinic compounds reported here, cyclodimerization of olefins,^{17,30} stereomutation of olefins,³¹ oxidation of leuco crystal violet,³² and ring cleavage of cyclobutane compounds.^{1,20}

Experimental Section

Materials. Spectral grade acetonitrile was distilled 3 times from phosphorus pentoxide and then twice from calcium hydride before use. Methanol was distilled from magnesium methoxide before use. Furan, 2-methylfuran, and 2,5-dimethylfuran were distilled from sodium under a nitrogen atmosphere before use. Indene, 1,1-diphenylethylene, 1,3- and 1,4-dimethylnaphthalenes, anisole, o- and p-methylanisoles, 1,3,5-trimethoxybenzene, and o-dimethoxybenzene were distilled from sodium in vacuo before use. p-Dimethoxybenzene was distilled from sodium in vacuo and then recrystallized from hexane-benzene. Triethylamine was refluxed over and distilled from potassium hydroxide before use. The aromatic hydrocarbons were recrystallized 3 times from methanol or ethanol-benzene mixtures and then sublimed. p-Dicyanobenzene was purified by recrystallization from benzene and sublimation. All other chemicals and solvents were reagent grade and purified by distillation and/or recrystallization.

Analytical Methods. Melting points were taken on a hot stage and are uncorrected. Analytical gas-liquid chromatography (GLC) was performed on a Shimadzu GC-3BF dual-column instrument with flame ionization detectors. The 75 cm \times 4 mm column used for quantitative analyses of 1-methoxy-2,2-diphenylethane (7) and 2-methoxyindan (13) employed 10% Ucon Oil LB-550X on Neopak 1A. GLC analyses of the other products, the aromatic hydrocarbons, and p-dicyanobenzene were carried out with 75 cm × 4 mm columns packed with 5% PEG 20M on Shimalite W, 5% Ucon Oil LB-550X on Shimalite W, 3% SE-30 on Shimalite W, and 5% PEG-HT on Chromosorb WAW DMCS.

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded at 100 MHz on a JEOL JNM-PS-100 spectrometer and ¹³C NMR spectra on a JEOL JNM-FX-100 spectrometer. The solvent was chloroform-d. The chemical shifts are in δ , measured downfield from tetramethylsilane internal standard. Infrared (IR) spectra were obtained on a Shimadzu IR-400 spectrophotometer as Nujol mulls or solutions in carbon tetrachloride or chloroform. Ultraviolet spectra were obtained on a Hitachi 124 spectrophotometer. Fluorescence meausrments were carried out on a Hitachi MPF-2A fluorometer. Mass spectra were obtained on a Hitachi RMU-6E instrument.

Oxidation potentials were measured for N2-saturated acetonitrile solutions (10⁻³ M) vs. an Ag/Ag⁺ reference electrode at 23 \pm 0.1 °C by cyclic voltammetry. Details on measurements were identical with those described previously.^{20b} In most cases, voltammograms showed no cathodic peaks corresponding to reversible reduction of cation radicals. Therefore, half-peak potentials were employed as the half-wave oxidation potentials.

Quantum yields were determined for thoroughly degassed solutions, using 2-hexanone actinometer.³³ Potassium chromate solutions of different concentrations were used for isolation of the 313-nm light and change of the light intensity. Details of measurements were identical with those described previously.^{20b}

Elemental analyses were performed at the Elemental Analysis Center of The Institute of Scientific and Industrial Research, Osaka University.

Redox-Photosensitized Reaction of Furan in 4:1 Acetonitrile-Methanol. A 4:1 acetonitrile-methanol solution (150 mL) of furan (9.0 g, 132 mmol), P (0.2 g, 1.1 mmol), and DCNB (2.0 g, 16 mmol) in a Pyrex vessel was bubbled with a nitrogen stream for 30 min and then irradiated with a high-pressure mercury lamp (Eikosha, PIH-300) for 20 h under cooling with water at 20 ± 1 °C. After evaporation, hot hexane was added to the residue. Filtration gave 0.3 g of DCNB. After evaporation of the filtrate, vacuum distillation gave 1 (1.96 g, 74% yield based on unrecovered DCNB). Column chromatography of the residue on silica gel (70-230 mesh, Merck) gave 0.17 g of P (85% recovery). Compound 1 was recrystallized from methanol: mp 50-51 °C; IR 2220 (CN), 1640 (C=C), 1044 (C-O) cm⁻¹; ¹H NMR δ 3.42 (s, 3 H), 3.84 (ddd, J = 2.4, 2.2, 1.6 Hz, 1 H), 5.04 (dt, J = 2.2, 0.5 Hz, 1 H), 5.08 (ddd, J = 3.0, 2.4, 2.2 Hz, 1 H), 6.50 (ddd, J = 3.0, 1.6, 0.5 Hz, 1 H), 7.20-7.62 (A₂B₂, 4 H); ¹³C NMR δ 54.8, 55.8, 103.5, 111.1, 111.9, 118.7, 128.3–132.5 (4 C), 145.6, 146.2; mass spectrum, m/e 201 (M⁺).

Anal. Calcd for C₁₂H₁₁NO₂: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.58; H, 5.34; N, 7.04.

Conversion of 1 to 2-(4-Cyanophenyl) furan. A benzene solution (5 mL) of 1 (0.5 g, 2.5 mmol) was added into a column packed with 20 g of silica gel and allowed to stand overnight. Elution with 20% benzene in hexane gave 2-(4-cyanophenyl)furan (0.24 g, 70% yield based on unrecovered 1). Unreacted 1 (0.1 g) was recovered by elution with 30% benzene in hexane. The furan compound was recrystallized from methanol: mp 65-66 °C; IR 2240, 1630, 1030 cm⁻¹; ¹H NMR § 6.42 (dd, J = 3.8, 1.9 Hz, 1 H), 6.65 (d, J = 3.8 Hz, 1 H), 7.43 (d, J = 1.9 Hz, 1 H), 7.46–7.69 (A₂B₂, 4 H); mass spectrum, m/e 169 (M⁺).

Anal. Calcd for C₁₁H₇NO: C, 78.09; H, 4.17; N, 8.28. Found: C, 77.80; H, 4.22; N, 8.03.

Redox-Photosensitized Reaction of 2-Methylfuran in 4:1 Acetonitrile-Methanol. A 4:1 acetonitrile-methanol solution of 2 -methylfuran (9 g, 110 mmol), P (0.2 g, 1.1 mmol), and DCNB (2 g, 16 mmol) was irradiated for 20 h. After evaporation, hot hexane was added to the residue and then unreacted DCNB (0.26 g) was filtered off. The filtrate was chromatographed on silica gel. After elution of P (0.18 g) with hexane, 2-methyl-5-(4-cyanophenyl)furan (0.1 g, 4% yield) was eluted with 15% benzene in hexane, 2-methyl-2-methoxy-5-(4-cyanophenyl)-2,5-dihydrofuran (2) (1.55 g, 53% yield) with 20-30% benzene in hexane, and then 2-methoxy-3-(4-cyanophenyl)-5-methyl-2,3-dihydrofuran (3) (0.32 g, 11% yield) with 1:1 benzene-hexane. The ¹H NMR spectrum of 2, showed two singlets at δ 1.60 and 1.67 for the methyl group and at δ 3.39 and 3.42 for the methoxyl group. Compound 3 was recrystallized from methanol: mp 59-61 °C; IR 2220, 1660, 1050 cm⁻¹; ¹H NMR δ 1.16 (s, 3 H), 3.33 (s, 3 H), 3.77 (m, 1 H), 4.58 (m, 1 H), 4.89 (d, J =2.7 Hz, 1 H), 7.1-7.3 (A₂B₂, 4 H); mass spectrum, m/e 215 (M⁺). Anal. Calcd for C₁₃H₁₃NO₂: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.31; H, 5.80; N, 6.44.

Conversion of 2 to 2-Methyl-5-(4-cyanophenyl)furan. A benzene solution (2 mL) of 2 (0.5 g, 2.3 mmol) was added into a column packed with 20 g of silica gel and allowed to stand overnight. Elution with 20% benzene in hexane gave 2-methyl-5-(4-cyanophenyl)furan (0.25 g, 74% yield based on unrecovered 2). Unreacted 2 (0.1 g) was recovered by elution with 30% benzene in hexane. The furan compound was recrystallized from methanol: mp 82-83 °C; IR 2230, 1640, 1025 cm⁻¹; ¹H NMR δ 2.41 (s, 3 H), 5.97 (d, J = 3.0 Hz, 1 H), 6.55 (d, J = 3.0 Hz, 1 H), 7.45-7.69 (A₂B₂, 4 H); mass spectrum, m/e 183 (M⁺).

Anal. Calcd for C₁₂H₉NO: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.50; H, 4.82; N, 7.71.

Conversion of 2 to 1-(4-Cyanophenyl)-1,4-pentanedione. Hydrogenation of 2 over 5% palladium-carbon gave the corresponding tetrahydrofuran compound in almost quantitative yield. This compound (0.3 g, 1.4 mmol) was added to a diluted sulfuric acid made from 3 mL of concentrated sulfuric acid and 30 mL of water. This solution was refluxed for 2 h, then cooled to room temperature, and extracted with 100 mL of diethyl ether. The ether extract was washed with saturated sodium bicarbonate and brine, dried, and filtered. Evaporation and distillation gave an oil; bp 76 °C (0.1 mmHg). The ¹H NMR spectrum of this oil showed two singlets at δ 1.42 and 1.62 for the methyl group and a broad signal at δ 3.65 for hydroxylic proton. To an acetone solution of this oil (0.2 g/5 mL) was added dropwise a diluted sufuric acid solution of chromium trioxide until the solution turned orange. After addition of 50 mL of diethyl ether, the ether solution was washed with saturated sodium bicarbonate and brine, dried, and filtered. After evaporation, the residue was chromatographed on silica gel; elution with benzene gave the diketone: mp 175-177 °C (from benzene-hexane); IR 2220, 1730 cm⁻¹; ¹H NMR δ 1.79 (s, 3 H), 2.65 (m, 4 H), 7.61-7.94 (A₂B₂, 4 H); mass spectrum, m/e 201 (M⁺).

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Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.50; H, 5.44; N, 6.70.

Redox-Photosensitized Reaction of 2,5-Dimethylfuran in 4:1 Acetonitrile-Methanol. A 4:1 acetonitrile-methanol solution of 2,5-dimethylfuran (10 g, 104 mmol), P (0.2 g, 1.1 mmol), and DCNB (2 g, 16 mmol) was irradiated for 20 h. After evaporation, hot hexane was added and then unreacted DCNB (0.93 g) was filtered off. The filtrate was chromatographed on silica gel. After elution of P (0.17 g) with hexane, 2,5-dimethyl-2-methoxy-5-(4-cyanophenyl)-2,5-dihydrofuran (4) (0.15 g, 8% yield) was eluted with 20% benzene in hexane and then 2,5-dimethyl-2-methoxy-3-(4-cyanophenyl)-2,3-dihydrofuran (5) (0.60 g, 31% yield) with 40% benzene in hexane. Both 4 and 5 did not solidify. The ¹H NMR spectrum of 4 showed two singlets at δ 3.36 and 3.40 for the methoxy group, demonstrating that 4 is a mixture of the cis and trans isomers. On the other hand, 5 is either the cis or trans isomer: bp 103 °C (0.05 mmHg); IR 2220, 1630, 1020 cm⁻¹; ¹H NMR δ 1.18 (s, 3 H), 1.60 (br, s, 3 H), 3.39 (s, 3 H), 3.86 (m, 1 H), 4.62 (d, J = 2.1 Hz; 1 H), 7.15-7.45 (A₂B₂, 4 H).

Conversion of 4 to 5-Hydroxy-5-(4-cyanophenyl)-2-hexanone. The ketol was obtained from 4 in 60% yield according to the procedures employed for the conversion of 2 to the corresponding diketone and was recrystallized from chloroform-benzene: mp 116-118 °C; IR 3430, 2220, 1740 cm⁻¹; ¹H NMR δ 1.46 (s, 3 H), 1.80 (s, 3 H), 2.70 (m, 4 H), 3.33 (br s, 1 H), 7.70-7.95 (A₂B₂, 4 H); mass spectrum, *m/e* 217 (M⁺).

Anal. Calcd for C₁₃H₁₅NO₂: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.66; H, 6.70; N, 6.40.

Conversion of 5 to 3-(4-Cyanophenyl)-2,5-hexanedione. In a similar way, 5 was converted to the diketone: mp 179–180 °C (from benzene-hexane); IR 2220, 1740 cm⁻¹; ¹H NMR δ 1.77 (s, 3 H), 1.82 (s, 3 H), 3.09 (d, J = 4.6 Hz, 2 H), 4.85 (t, J = 4.6 Hz, 1 H), 7.56–7.90 (A₂B₂, 4 H); mass spectrum, m/e 215 (M⁺).

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 5.51. Found: C, 72.31; H, 5.82; N, 6.44.

Redox-Photosensitized Reaction of 1,1-Diphenylethylene in Acetonitrile. An acetonitrile solution of 1,1-diphenylethylene (1.0 g, 5.6 mmol), P (0.2 g, 1.1 mmol), and DCNB (2 g, 16 mmol) was irradiated for 20 h. After evaporation, hot hexane was added to the residue and then unreacted DCNB (1.8 g) was filtered off. The filtrate was chromatographed on silica gel. After elution of P (0.17 g) with hexane, a solid was eluted with 30% benzene in hexane. Recrystallization from methanol gave pure 1,1,4-triphenyltetralin (0.89 g, 89% yield based on DPE used): mp 121-122 °C; ¹H NMR δ 1.60-2.10 (m, 2 H), 2.64 (br t, J = 4.8 Hz, 2 H), 4.16 (t, J = 7.5 Hz, 1 H), 6.88-7.40 (7, 19 H); ¹³C NMR δ 29.73, 36.84, 46.25, 54.09, 122.6-131.6 (19 C), 139.8, 143.0, 147.8, 148.0, 148.9; mass spectrum, m/e 360 (M⁺).

Anal. Calcd for $C_{28}H_{24}$: C, 93.29; H, 6.71. Found: C, 93.10; H, 6.55.

Redox-Photosensitized Reaction of 1,1-Diphenylethylene in Acetonitrile-Methanol. A 4:1 acetonitrile-methanol solution of 1,1-diphenylethylene (1.0 g, 5.6 mmol), P (0.2 g, 1.1 mmol), and DCNB (2 g, 16 mmol) was irradiated for 20 h. After evaporation, hot hexane was added to the residue and then unreacted DCNB (1.85 g) was filtered off. After evaporation of the filtrate, vacuum distillation gave 1-methoxy-2,2-diphenylethane (0.82 g, 70% yield): bp 130 °C (10 mmHg); IR 1110 cm⁻¹; ¹H NMR δ 3.28 (s, 3 H), 3.78 (d, J = 6.9 Hz, 2 H), 4.16 (t, J =6.9 Hz, 1 H), 7.10 (m, 10 H); ¹³C NMR δ 51.02, 58.77, 75.97, 127.6-132.5 (10 C), 142.1, 142.4; mass spectrum, m/e 212 (M⁺).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.91; H, 7.61.

The residue of the distillation was chromatographed on silica gel; after elution of P (0.18 g) with hexane, a solid was eluted with 1:1 benzenehexane. Recrystallization from ethanol gave pure 1-methoxy-1,1,4,4tetraphenylbutane (0.2 g, 9% yield): mp 135–136 °C; IR 1060 cm⁻¹; ¹H NMR δ 1.90 (t, J = 5.5 Hz, 2 H), 2.12 (dt, J = 5.5, 7.0 Hz, 2 H), 2.88 (s, 3 H), 3.68 (t, J = 7.0 Hz, 1 H), 7.0–7.2 (m, 20 H); ¹³C NMR δ 28.07, 33.33, 51.51, 82.30, 92.10, 126.1–131.1 (20 C), 144.97 (2 C), 145.36 (2 C); mass spectrum, m/e 392 (M⁺).

Anal. Calcd for $C_{29}H_{28}O$: C, 88.73; H, 7.19. Found: C, 88.82; H, 7.16.

Redox-Photosensitized Reaction of Indene in Acetonitrile–Water. A 4:1 acetonitrile–water solution of indene (10 g, 86 mmol), P (0.5 g, 2.8 mmol), and DCNB (2 g, 16 mmol) was irradiated for 20 h. After removal of two-thirds of the solvent, the remainder was added into 300 mL of chloroform, and then the organic layer separated was dried. After filtration and evaporation, vacuum distillation gave 1.82 g of indene and 6.64 g of 2-indanol (9) (mp 68–69 °C, ⁵⁶ 70% yield based on unrecovered indene). The residue was chromatographed on silica gel and the following compounds were eiluted in turn with mixtures of benzene and hexane: P (0.44 g) with hexane, DCNB (0.92 g) with 10% benzene in hexane, 1-(4-cyanophenyl)-2-indanol (10) (0.64 g, 33% yield based on unrecov-

ered DCNB) with 20% benzene in hexane, 1-hydroxy-1'-(4-cyanophenyl)-2,2'-biindanyl (11) (1.18 g, 40% yield based on unrecovered DCNB) with 40% benzene in hexane, and 1-hydroxy-2,2'-biindanyl (12) (0.89 g, 10% yield based on unrecovered IN) with 1:1 benzene-hexane. Compound 11 was recrystallized from methanol: mp 180–180.5 °C; IR 3620, 2230, 1130 cm⁻¹; ¹H NMR δ 1.81 (br s, 1 H), 2.1–2.3 (m, 6 H), 4.28 (d, J = 8.8 Hz, 1 H), 4.95 (d, J = 6.3 Hz, 1 H), 6.62 (m, 1 H), 6.8–7.25 (m, 7 H), 7.25–7.4 (A₂B₂, 4 H); ¹³C NMR δ 35.1, 36.0, 53.2, 53.5, 56.1, 79.1, 110.0, 118.7, 123.5, 124.1, 124.3, 126.6 (2 C), 126.9, 127.9, 129.1, 129.4 (2 C), 132.0 (2 C), 140.8, 142.5, 144.2, 145.5, 150.32; mass spectrum, m/e 351 (M⁺, vw), 333 (M – H₂O), 218, 133, 115.

Anal. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99. Found: C, 85.17; H, 5.96; N, 3.89.

Compound 12 was recrystallized from ethanol-benzene, mp 182–183 °C.^{5b} On the other hand, 10 did not solidify: IR 3600, 2230, 1230 cm⁻¹; ¹H NMR δ 1.90 (br s, 1 H), 2.60–3.26 (m, 2 H), 4.10 (dt, J = 7.2, 6.8 Hz, 1 H), 4.28 (d, J = 7.2 Hz, 1 H), 6.7–7.5 (m, 8 H).

Conversion of 10 to Methyl 2-(4-Cyanobenzoyl)phenylacetate. To an acetone solution (10 mL) of 10 (0.6 g) was added dropwise a solution of chromium trioxide in diluted sulfuric acid until the solution turned orange and then 100 mL of diethyl ehter was added. The ether layer was washed with brine and dried. After condensing the ether solution to ~10 mL, a diethyl ether solution of diazomethane was added dropwise into the condensed solution. After evaporation, the solid residue was recrystallized from ethanol to give pure methyl 2-(4-cyanophenyl)benzoylacetate (0.5 g): mp 63-65 °C; IR 2220, 1740, 1210 cm⁻¹; ¹H NMR δ 3.62 (s, 3 H), 3.84 (s, 2 H), 7.2-7.5 (m, 4 H), 7.65-7.83 (A₂B₂, 4 H); UV (benzene) λ_{max} (log ϵ) 345 nm (3.38); mass spectrum, *m/e* 279 (M⁺).

Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 72.89; H, 4.51; N, 4.87.

Redox-Photosensitized Reaction of Indene in Acetonitrile-Alcohol. As a typical run, the photoreaction in 4:1 acetonitrile-methanol will be described. A solution of indene (10 g, 86 mmol), P (0.5 g, 2.8 mmol), and DCNB (2 g, 16 mmol) was irradiated for 20 h. After removal of the solvent, vacuum distillation gave unreacted indene (0.66 g) and 2methyoxyindan (8.2 g, 69% yield based on unrecovered IN). The residue was chromatographed on silica gel. The following compounds were eluted in turn with hexane or with mixtures of benzene-hexane; P (0.48 g) with hexane, DCNB (0.61 g) with 10% benzene in hexane, 1-(4cyanophenyl)-2-methoxyindan (14) (2.2 g, 80% yield based on unrecovered DCNB) with 30% benzene in hexane, and then 2,2'-dimethoxy-1,1'-biindanyl (15) (1.9 g, 16% yield based on unrecovered IN) with benzene. Compound 14 was recrystallized from methanol: mp 90–91 °C; IR 2230, 1020 cm⁻¹; ¹H NMR δ 2.89 (dd, J = 15, 6.8 Hz, 1 H), 3.34 (dd, J = 15, 6.8 Hz, 1 H), 3.29 (s, 3 H), 4.09 (q, J = 6.8 Hz, 1 H), 4.31 (d, J = 6.8 Hz, 1 H), 6.77 (m, 1 H), 7.12 (m, 3 H), 7.25–7.5 (A₂B₂, 4 H); mass spectrum, m/e 249 (M⁺).

Anal. Calcd for $C_{17}H_{15}NO:\ C,\, 81.90;\ H,\, 6.06;\ N,\, 5.62.$ Found: C, 81.86; H, 5.97; N, 5.55.

Similarly, 4:1 acetonitrile-alcohol solutions were irradiated for 20 h. After evaporation of the solvent, vacuum distillation gave 2-alkoxyindan. No efforts for isolation and identification of other products were made.

2-Ethoxyindan: bp 85-89 °C (5 mmHg); ¹H NMR δ 1.14 (t, J = 7 Hz, 3 H), 2.97 (m, 4 H), 3.48 (q, J = 7 Hz, 2 H), 4.24 (q, J = 5.8 Hz, 1 H), 7.04 (m, 4 H); mass spectrum, m/e 162 (M⁺).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.22; H, 8.44.

2-Isopropoxyindan: bp 36-40 °C (0.05 mmHg); ¹H NMR δ 1.09 (d, J = 5.8 Hz, 6 H), 2.90 (m, 4 H), 3.57 (m, 1 H), 4.26 (q, J = 6 Hz, 1 H), 6.93 (m, 4 H); mass spectrum, m/e 176 (M⁺).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.94; H, 8.91.

2-tert-Butoxyindan: bp 117 °C (0.01 mmHg); ¹H NMR δ 1.15 (s, 9 H), 2.87 (m, 4 H), 4.35 (q, J = 6.3 Hz, 1 H), 6.9 (m, 4 H); mass spectrum, m/e 190 (M⁺).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.94; H, 9.32.

2-Cyclohexyloxyindan: bp 93-94 °C (0.01 mmHg); ¹H NMR δ 1.04-1.93 (m, 10 H), 2.94 (m, 4 H), 3.30 (m, 1 H), 4.37 (q, J = 6.4 Hz, 1 H), 7.01 (m, 4 H); mass spectrum, m/e 216 (M⁺).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.46; H, 9.21.

2-Benzyloxyindan: bp 129–132 °C (0.005 mmHg); ¹H NMR δ 2.94 (m, 4 H), 4.22 (q, J = 6.6 Hz, 1 H), 4.36 (s, 2 H), 6.9–7.1 (m, 9 H); mass spectrum, m/e 224 (M⁺).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.96; H, 6.95.

Direct Photoreaction of Indene with DCNB in Acetonitrile-Methanol. A 4:1 acetonitrile-methanol solution of indene (10 g, 86 mmol) and DCNB (2 g, 16 mmol) was irradiated for 60 h. After removal of the solvent, vacuum distillation gave unreacted indene (4.1 g) and 2-methoxyindan (2.4 g, 30% yield based on unrecovered indene). Column chromatography of the distillation residue on silica gel gave DCNB (1.0 g) and 14 (0.8 g, 40% yield based on unrecovered DCNB). Considerable amounts of heavy oils (~ 4 g) were eluted with benzene and then with 20% ethyl acetate in benzene. The oils were combined and then distilled in vacuo to give 15 (1.5 g, 20% yield based on unrecovered indene); bp 160-163 °C (0.1 mmHg).

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Mechanism of Hydrolysis of N-(1-Aminoalkyl) Amides¹

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Abstract: Many of the title compounds (structure 1) are remarkably stable to hydrolysis and can be isolated and characterized. The pH-rate profile for hydrolysis of the title compounds involves plateaus in the acid and base region, with the rates of hydrolysis in the basic region somewhat faster. The compounds hydrolyze to amides, aldehydes, and ammonia; the intermediacy of an imine in the basic region is demonstrated by its trapping with added CN⁻. An optically active derivative of 1 hydrolyzes and loses optical activity at about the same rate in both the acidic and basic regions of pH. The reaction is characterized in basic solution by highly positive activation entropies, and alkylation of the amino nitrogen increases the rate significantly. The hydrolysis reaction shows no detectable buffer catalysis at any pH studied. The hydrolysis reaction is very sensitive to the amide leaving group; electron-withdrawing substituents on the amide portion of 1 substantially increase the rate of hydrolysis. The mechanism of hydrolysis in basic solution seems to be best described as a unimolecular solvolysis with an amide anion as a leaving group (Scheme I). In acidic solution the most likely mechanism of hydrolysis (Scheme II) appears to involve the expulsion of an amide enol (imidic acid). The implications of these findings are discussed for situations in which compounds of type 1 have found utility.

Compounds of type 1 have emerged as important entities in

the peptide area in recent years. Goodman and his co-workers² have used such species as "mock" amino termini in the con-struction of several "retro-inverso" peptides. In such peptides, the $N \rightarrow C$ sequence of a normal peptide containing L amino acids has become the $C \rightarrow N$ sequence containing D amino acids. The result of this molecular "double-reverse" is that the retro-inverso peptide has in principle a side-chain topology similar to or identical with that of the natural peptide. The reversal of the amino and carboxyl terminus of such a peptide requires that groups be found which, simplistically stated, give the carboxyl terminus the appearance of the amino terminus, and vice versa. Despite the fact that peptides and their retro-enantiomers may not be rigorously correspondent,^{3a} the concept appears to offer considerable pharmacological promise. A group closely related to 1 has been used as a new amino protecting group for introducing dipeptide synthons^{3b} in peptide synthesis. The compound N^5 , N^{10} methylenetetrahydrofolate, which serves as a biochemical onecarbon shuttle from serine to methionine, features the N-C-N linkage, and a study of the breakdown of geminal diamines has been reported by several groups.⁴ Finally, compounds of type

1 have proven to be stable intermediates in our carboxyl-terminal peptide degradation.⁵

Compounds of type 1 other than those derived from formaldehyde⁶ were essentially unknown in the literature until Bergmann and Zervas⁷ encountered them as isolable intermediates when they thermally rearranged acyl amino acid azides in benzyl alcohol and hydrogenolyzed the resulting carbamates. These authors noted that such compounds are sufficiently stable to be isolated in crystalline form, and further noted that the compounds were interesting and deserved additional investigation. Despite these comments, these derivatives have not reemerged in the literature until the recent past. One reason for this may be that these compounds are rather thinly veiled aldehydes; they are nitrogen analogs of "hemiacylals". One might naively have expected these compounds to be highly unstable but such is, in fact, not the case.

In order that the use of these compounds be optimized, a knowledge of their properties-in particular, their hydrolytic stability-is essential. In addition, the reasons for the hydrolytic stability are of interest. We here report our study on the mechanism of hydrolysis of the N-(1-aminoalkyl) amides 2-4.

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