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Photo-Induced Friedel-Crafts Acylation of Anthracene with Aroyl Chlorides

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The photo-excitation of anthracene (**1**) in the presence of benzoyl chloride and its *p*- or *m*-substituted compounds (**2**) gave the corresponding 2- and 9-aroylanthracenes. No isomeric 1-aroylanthracenes (**3**) were detected. The aroyl chlorides (**2**) were found to quench the fluorescence of **1**. The quenching constants obtained increased with increasing electron-withdrawing ability of the substituents and are in agreement with those independently obtained from the quantum yield determinations. The efficiency of the photoaroylation was dependent on the solvent polarity. The results suggest a plausible photochemical mechanism, which involves a CT complex formed from **1** in the excited singlet state and **2** in the ground state. This complex formation is supported by the positional selectivity exhibited in the product distribution.

Few papers concerning photo-induced Friedel-Crafts reactions have been published.[1-5] The photochemical mechanisms differ from case to case. For the photoacetylation of benzene with trifluoroacetic acid, an ionic intermediate was assumed.[1b] The photoalkylation of the phenyl nucleus with chloroacetyl derivatives occurs through a radical reaction,[2] while, in the presence of metallic halides, electrophilic substitution prevails.[3] Recently, positional selectivity was reported for the photobenzoylation of anthracene (**1**) with benzoyl chloride (**2d**): substitution on the aromatic ring preferentially occurs at positions 2 and 9, but scarcely at position 1.[5] This paper describes further results for photoaroylation and discusses the photochemical mechanisms.

Continuing attention has been focused on the exciplex formation between electron-rich aromatics and compounds containing an activated C–Cl or similar bond.[6] It is supposed for these systems that the chemical reactivity of the C–Cl bond plays an important role in the quenching process, although CT interaction is primarily responsible for association of an exciplex. The quenching mechanisms may be related to the case described here.

Results

Photoaroylation. The absorption spectra of a mixed solution of anthracene (**1**) and benzoyl chloride (**2d**) are shown in Fig. 1a. No new absorption bands are seen before irradiation. The solution was exposed to 365 nm mercury light in a nitrogen atmosphere. The irradiating light was absorbed by **1**, but not by the aroyl chlorides (**2**), the absorbance of **2** being negligible

TABLE 1. CHARACTERISTICS OF THE PRODUCTS FORMED FROM THE PHOTOAROYLATION OF ANTHRACENE

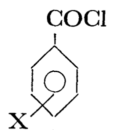
Product	Yield[a] (%)	Mp (°C)	$\nu_{\max}$[d] (cm^{-1})	δ[e] (ppm)	Coloration[f] with H_2SO_4	Emission in EtOH ($\lambda_{\max}$ in nm)
4a	29	189—190		3.9(3H)	P	502
4b	23	183—185		2.4(3H)	P	498
4c	27	158—159		2.4(3H)	P	520
4d	19	169—171[b]			P	523
4e	30	211—213			P	523
4f	30	140—142		3.8(3H)	P	522
4g	28	200—202			P	510
4h	29	223—224			P	538
4i	24	198—199	2220(CN)		V	544
4j	19	191—193	2220(CN)		V	560
5a	30	185—186		3.75(3H)	V	—[g]
5b	53	125—126		2.9(3H)	PB	—
5c	36	131—133		2.25(3H)	G	—
5d	47	145—146[c]			PB	—
5e	37	162—163			PB	—
5f	51	155—158		3.7(3H)	G	—
5g	34	186—188			PB	—
5h	58	139—141			PB	—
5i	56	155—157	2230(CN)		PB	—
5j	11	217—218	2220(CN)		G	—

a) Relative to anthracene loss (60% conversion). b) Lit,[29] 175 °C. c) Lit,[28] 148 °C. d) 1650—1670 cm^{-1} (C=O), except as noted. e) 8.4—8.5 (2H, Ar) and 7.0—8.4 (Ar) for a series of compounds of **3**; 8.5—8.7 (1H, Ar) and 6.8—8.3 (Ar) for a series of compounds of **4**, except as noted. f) P, purple; V, violet; PB, Prussian blue; G, green. g) No emission.

above 340 nm. The major products obtained were identified, by comparison with anthentic species, to be 2- (**4d**) (19% in benzene and 24% in acetonitrile based on the amount of **1** consumed) and 9-benzoylanthracene (**5d**) (47% in benzene and 57% in acetonitrile). No isomeric 1-benzoylanthracene (**3d**) was detected. Other aroyl chlorides (**2a**—**c** and **e**—**j**) gave the corresponding products under appropriate conditions. The product yields were 20—30% for **4**, 30—60% for **5**, as listed in Table 1, and trace or nil amounts for **3**.

Besides the ketonic compounds, anthracene photodimer was also formed with less yields (10—20%) than that in the absence of **2**. Added dry hydrogen chloride prevented photoaroylation and caused the chlorination of **1**. In an oxygen stream, photoaroylation was repressed (**4d**, 5%; **5d**, 10%) and anthraquinone was formed as a major product (40%).

In the case of **2d** in acetonitrile, irradiation was also performed with the 254 nm light, which was absorbed by all starting materials. The same ketonic products, **4d** (5%) and **5d** (40%), and in addition 9,10-dibenzoylanthracene (15%) were formed. The yield of **4d** is remarkably small compared with that for 365 nm light irradiation.



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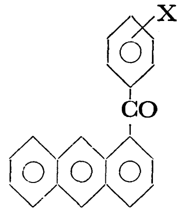

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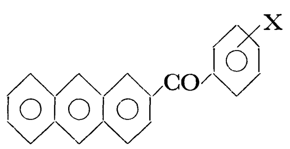

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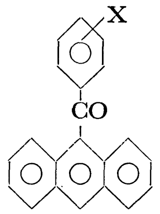

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a, X=*p*-CH_3O **e**, X=*p*-F **i**, X=*m*-CN
b, X=*p*-CH_3 **f**, X=*m*-CH_3O **j**, X=*p*-CN
c, X=*m*-CH_3 **g**, X=*p*-Cl
d, X=H **h**, X=*m*-Cl

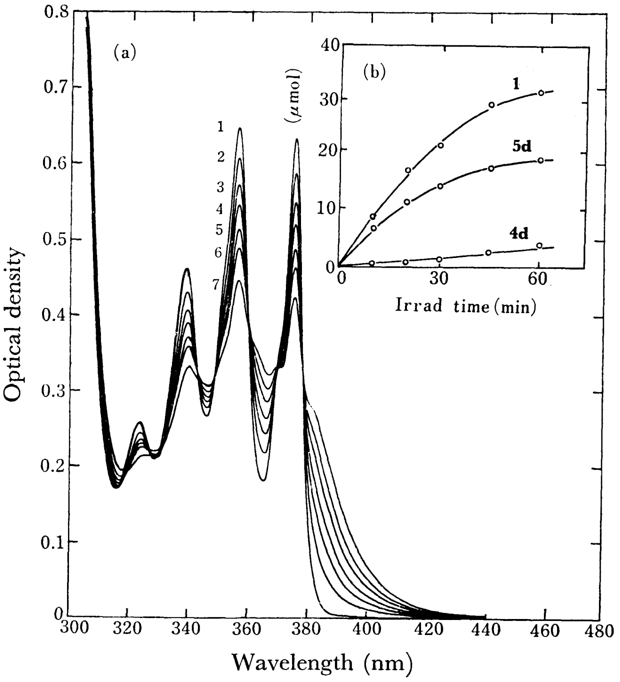


Fig. 1. (a) Absorption spectra during irradiation: (1) 0, (2) 10, (3) 20, (4) 30, (5) 45, (6) 60, (7) 90 min, (b) Conversion curves based on the spectral changes on the assumption that anthracene (**1**), 2-, (**4d**), and 9-benzoylanthracene (**5d**) are responsible for the spectra.

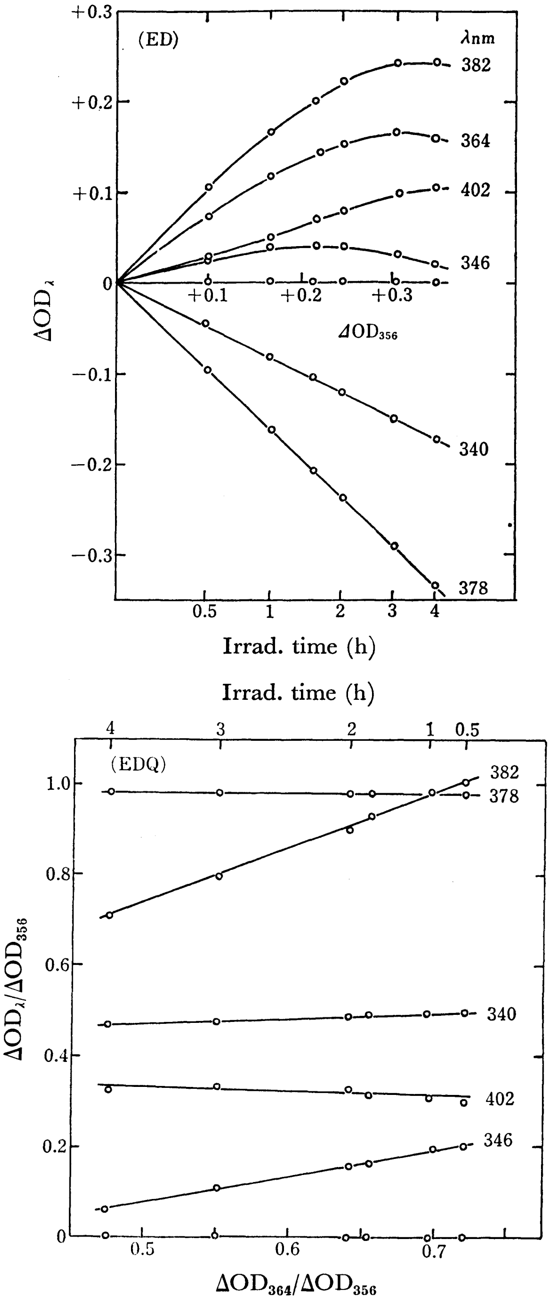


Fig. 2. Extinction difference (ED) and extinction difference quotient (EDQ) diagrams of the absorption spectra.

Reaction Pathway. In order to elucidate the reaction pathway of the photoaroylation, the extinction difference (ED) and extinction difference quotient (EDQ) diagrams[7] are plotted in Fig. 2, using the spectral data shown in Fig. 1a. The ED diagram shows linear curves at all wavelengths until about one-half of the starting amounts of **1** had been consumed. These linear relations suggest that the photoreaction proceeds only *via* a one-step reaction, *i.e.*, **1**+**2**→one product or products with a constant yield ratio. Since both isomeric ketones, **4d** and **5d**, are formed immediately after irradiation, as is shown in Fig. 1b, it can be concluded that these compounds are simultaneously produced by a bimolecular reaction of **1** and **2**. The product yield ratio of **4d** to **5d** is *ca.* 0.1 at the initial stage of the photoreaction, as is shown in Fig. 1b.

For more prolonged irradiation periods, the ED plots deviate from linear relations, particularly at wavelengths of the **5d** peak maxima (346, 364, and 382 nm). However, all the EDQ plots remain linear up to nearly complete consumption of **1**. This indicates that **5d** formed undergoes a subsequent chemical change, while **4d** unchanges. In a preliminary experiment, it was found that irradiation of **5d** in benzene gave none of the isomeric ketones, but gave a photodimer analogous to those derived from **1** or its meso substituted compounds.[8] Consequently, the photodimerization may be mainly responsible for the loss of **5** during the course of photoaroylation. The possibility of the isomerization reaction can be excluded.

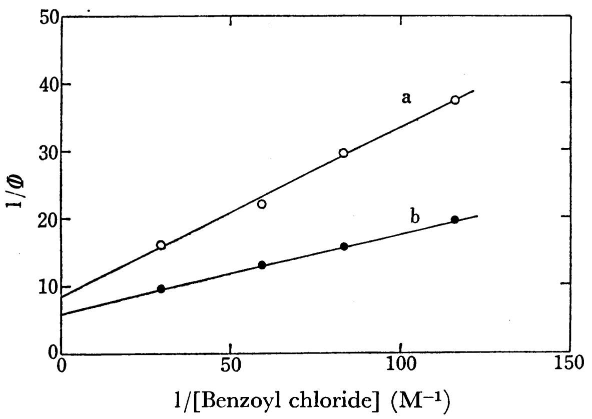


Fig. 3. Concentration dependency of the quantum yield for the loss of anthracene: (a) in benzene and (b) in acetonitrile.

Quantum Yields. The loss of **1** is dependent on the aroyl chloride concentration, as is shown in Fig. 3, where the reciprocals of the quantum yields for the disappearance of **1** are plotted against the reciprocals of the benzoyl chloride concentrations. Values of the products of the limiting quantum yield and the quenching constant, $k_q\tau$ (the ratio of intercept to slope), are listed in Table 2. Although the values of the limiting quantum yield are about the same for most reactions of **2** in benzene, they become much more enhanced in acetonitrile for the aroyl chlorides which have an electron-withdrawing substituent. On the contrary, the electron-repelling substituents relatively depress the quantum yield in acetonitrile.

Table 2. The limiting quantum yields and quenching constants in the photoaroylation of anthracene

Aroyl chloride		Solvent			
		Benzene		Acetonitrile	
		Φ_∞ [a]	$k_q\tau$ [b] (M⁻¹)	Φ_∞ [a]	$k_q\tau$ [b] (M⁻¹)
p-CH$_3$O	(**2a**)	0.12	11	<0.03[c]	c
p-CH$_3$	(**2b**)	0.15	30	0.11	40
m-CH$_3$	(**2c**)	0.13	39	0.12	69
H	(**2d**)	0.12	35	0.16	62
p-F	(**2e**)	0.13	40	0.15	74
m-CH$_3$O	(**2f**)	d	d	d	d
p-Cl	(**2g**)	0.13	39	0.21	98
m-Cl	(**2h**)	0.12	48	0.31	75
m-CN	(**2i**)	<0.03[c]	c	0.18	89
p-CN	(**2j**)	<0.01[c]	c	0.06	170

a) The limiting quantum yield determined from the intercept in the $1/\Phi$ *vs.* $1/[Q]$ plots. b) Determined from the ratio of intercept to slope. c) Not determined to good precision due to less reactivity. d) Not determined due to internal filter effect of *m*-methoxybenzoyl chloride.

Table 3. Fluorescence quenching data

Aroyl chloride		Solvent			
		Benzene		Acetonitrile	
		$k_q\tau$ [a] (M⁻¹)	$10^{-9}k_q$ [b] (M⁻¹ s⁻¹)	$k_q\tau$ [a] (M⁻¹)	$10^{-10}k_q$ [b] (M⁻¹ s⁻¹)
p-CH$_3$O	(**2a**)	15	3.1	61	1.2
p-CH$_3$	(**2b**)	29	5.9	68	1.3
m-CH$_3$	(**2c**)	35	7.1	71	1.4
H	(**2d**)	38	7.8	78	1.5
p-F	(**2e**)	38	7.8	78	1.5
m-CH$_3$O	(**2f**)	38	7.8	71	1.4
p-Cl	(**2g**)	46	9.4	82	1.6
m-Cl	(**2h**)	48	9.7	88	1.7
m-CN	(**2i**)	56	11	95	1.8
p-CN	(**2j**)	62	13	110	2.1

a) The slope of the Stern-Volmer plots for an excitation wavelength of 380 nm. b) Determined from the singlet lifetime of anthracene: τ 4.9 ns in benzene and 5.3 ns in acetonitrile (Ref. 10).

Fluorescence Quenching. The Stern-Volmer plots were linear for most quenchers, **2**, while upward curvature was observed for **2i** and **j**. No new emission was detected in the presence of **2**. The values of $k_q\tau$ as determined from the initial slope and of the quenching rate constant, k_q, are listed in Table 3. The values of $k_q\tau$ obtained are in agreement with those obtained from the quantum yield determinations (Table 2) to within experimental errors. The k_q increases with increasing electron-withdrawing ability of the substituent and ultimately approaches the diffusion rate canstant, k_{diff}, which is equal to $1\times10^{10}\ \text{M}^{-1}\,\text{s}^{-1}$ in benzene and $1.8\times10^{10}\ \text{M}^{-1}\,\text{s}^{-1}$ in acetonitrile, as calculated using the Debye expression.[9] The upward curvatures in the

TABLE 4. QUANTUM YIELDS FOR DIRECT PHOTOLYSIS OF AROYL CHLORIDES

Aroyl chloride		Quantum yield
p-CH$_3$O	(**2a**)	0.046
H	(**2d**)	0.038
m-Cl	(**2h**)	0.029
m-CN	(**2i**)	0.016
p-CN	(**2j**)	0.033

Stern-Volmer plots and the large k_q values suggest that a ground-state complex is formed from **1** and the aroyl chlorides, the substituent of which is strongly electron-withdrawing (*vide infra*).

Direct Photolysis of Aroyl Chlorides. The quantum yields are listed in Table 4. The data indicate that **2** becomes more photostable when an electron-withdrawing substituent is introduced into the aroyl system. The trend of the substituent effect is distinctly different from that for photoaroylation. Furthermore, it is noteworthy that the quantum yields for direct photolysis are much smaller than the limiting quantum yields of the photoaroylation (the fourth column in Table 2).

Discussion

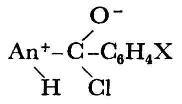
The agreement between the quenching constants obtained independently from the fluorescence and photochemical measurements indicates that the photoreaction occurs in the excited singlet state of **1**. As is shown in Fig. 1a, only a very weak absorption band of **2** overlaps with the fluorescence of **1**, the long wavelength absorption maxima of **2** lying in much higher energy regions (*ca.* 100 kcal/mol) than that of **1** (76 kcal/mol).[10] Therefore, it is difficult to consider that the excitation energy would be transferred to the quencher through classical mechanisms, such as trivial or resonance energy transfer.[11] If these mechanisms were operating, the photoaroylation efficiencies would be related to those for direct photolysis of the quenchers, because these quenching processes lead to the formation of excited quenchers. However, the substitution dependence of the two photoreactions is exactly opposite.

On the other hand, the increase in the quenching constant with increasing electron-abstracting ability of the aroyl system suggests that the quenching process involves an exciplex formed from the excited aromatic hydrocarbon and the quencher. The exciplex mechanism is well established for electron-donor-acceptor pairs, for which the energy transfer appears to be strongly endothermic.[12] This mechanism is favored for explaining the positional selectivity observed, as is discussed below.

Consequently, the photoreaction may conform to the following reaction scheme, which was postulated for singlet quenching by electron transfer,[13] thus

$$\begin{tikzcd}
{}^1\underset{\mathbf{1}}{\mathrm{An}^*} + \underset{\mathbf{2}}{\mathrm{Q}} \arrow[r, shift left, "k_{\mathrm{diff}}"] & \underset{\mathbf{6}}{[{}^1\mathrm{An}^* \cdots \mathrm{Q}]} \arrow[l, shift left, "k_{-\mathrm{q}}"] \arrow[r, "k_{\mathrm{e}}"] & \underset{\mathbf{7}}{[\mathrm{An}^{\delta+} \cdots \mathrm{Q}^{\delta-}]^*} \arrow[dl, "k_{\mathrm{r}}"'] \arrow[d, "k_{\mathrm{d}}"] \\
 & \text{Products} & \mathrm{An} + \mathrm{Q},
\end{tikzcd} \qquad (1)$$

where An and ^{1}An* denote **1** in the ground and excited singlet states, respectively, Q denotes the aroyl chlorides, [^{1}An*···Q] is a proximate pair in a solvent cage, [An$^{\delta+}$···Q$^{\delta-}$]* denotes an exciplex, and the k are rate constants. The exciplex is either deactivated through radiationless decay or transformed into a radical ion pair and/or a zwitterionic intermediate, **8**, which yields products by the elimination of hydrogen chloride.



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The validity of an exciplex is substantiated by the fact that the yield of **4d** decreased when the reaction solution was irradiated with the 254 nm light. Under these conditions, the fraction of the incident light which is absorbed by **1** is relatively small, the quencher being able to absorb extensive amounts of the light. Therefore, substitution through an exciplex may compete with that through an aroyl radical generated by direct photolysis of the quencher. The latter photoreaction predominantly gives **5d**, because the carbon atom at the meso position of **1** has the greatest reactivity. It appears likely that the inefficient formation of **4d** is a response to the decrease in the probability for exciplex formation.

Furthermore, the quenching effect by oxygen may support the existence of long-lived intermediates. Judging from the fact that the photooxidation of **1** is rather inefficient in benzene[14,15] and that the singlet lifetime of **1** is very short, especially under the reaction conditions, added oxygen would not be expected to interfere by quenching ^{1}An*, but to become involved by quenching long-lived exciplex and/or radical ions.

The solvent dependence of the photoreaction is consistent with the mechanisms proposed. The higher quantum and product yields in acetonitrile *vs.* benzene are due to a greater degree of solvent stabilization for the polar exciplex in a high polarity solvent than in a poor polarity solvent. In this respect, it appears surprising that **2i** and **2j** are rather inactive in the photoaroylation, in spite of their great efficiency for fluorescence quenching. This may be the consequence of the rapid formation of solvated radical ions, since they are strong electron acceptors.

This scheme leads to the modified Strern-Volmer equation,

$$\phi_f^\circ/\phi_f = 1 + k_q\tau[Q], \qquad (2)$$

where

$$k_q = \frac{k_{\mathrm{diff}}k_e}{k_{-q}+k_e}, \qquad (3)$$

ϕ_f and ϕ_f° are the fluorescence quantum yield in the presence and absence of the quencher, respectively, k_{diff} and k_{-q} are the rate constants for diffusive formation and for separation of a proximate pair (**6**), respectively, and k_e is the rate constant for electron transfer. The quantum yield of the photoreaction, Φ, is given by

$$\Phi = \frac{k_q\tau[Q]}{1+k_q\tau[Q]}\,\frac{k_r}{k_r+k_d}, \qquad (4)$$

where the first term on the right-hand side is the probability for exciplex formation, the second term is the fraction of the exciplex which gives the photoproducts, and k_r and k_d are the rate constants for chemical transformation and for degradation to the starting materials, respectively. The limiting quantum yield refers to the rate-constant ratio, $k_r/(k_r+k_d)$. The data are summarized in Tables 2 and 3.

It is assumed in the reaction scheme that an exciplex is formed irreversibly. This assumption is convenient for the quenching reaction which occurs with a nearly diffusion-controlled rate.[16] Since CT interaction is mainly responsible for exciplex binding,[12] a definite relation between the k_q values measured and the Hammett substituent constant, σ, is expected. Although the k_q values given in Table 3 cannot be linearly correlated with σ, probably owing to the levelling effect, it appears possible to apply the kinetic treatment developed by Evans to the nearly diffusion-controlled quenching process.[13] On the assumption that the rate constant for the diffusive separation of a proximate pair, k_{-q}, is a constant parameter which is determined only by the properties of the solvent,[13] a linear free-energy relation is derived from Eq. 3, thus

$$\ln \frac{k_q}{k_{diff}-k_q} = \ln \frac{k_e}{k_{-q}} \propto \Delta G^{\neq}, \qquad (5)$$

where $\Delta G^{\neq}$ is the free energy of activation for the electron-transfer process.

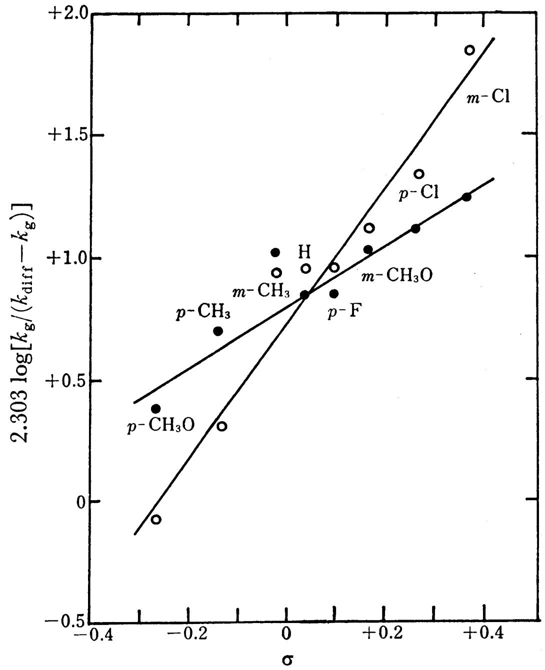

Fig. 4. Linear free-energy relation of the quenching constant: (○) in benzene and (●) in acetonitrile.

As is shown in Fig. 4, a linear relation is obtained between σ and the function, 2.303 $\log[k_q/(k_{diff}-k_q)]$, which was determined from the measured values of k_q and the calculated values of k_{diff}. The ρ values are 2.8 in benzene and 1.3 in acetonitrile. These positive ρ values strongly support CT interaction, in which electron transfer occurs from ^{1}An* to **2** in the ground state. The correctly linear relations shown in Fig. 4 confirm the validity of the reaction scheme proposed.

One should take account of a few possibilities for positional selectivity. First, there is the possibility that isomerization of the products gives rise to apparent positional selectivity. In fact, it is known that a variety of product distributions are produced in the thermal Friedel-Crafts acetylation of **1**, depending on the experimental conditions.[17] Substitution occurs prevalently at the meso position under mild conditions, whearas the acetyl group first attached at the meso position rapidly migrates to outer-ring positions under slightly drastic conditions and/or for prolonged reaction times. In contrast with the thermal reactions, the ketonic products in this system are formed from a bimolecular reaction of **1** and **2** without isomerization. Thus, the product-formation behavior is different from that in the ground-state reaction.

Second, the reactivity of the aromatic nucleus should be taken into account. As is known, low-lying excited singlet states of **1** consist of the ^1L_a and ^1L_b states, the former being much more abundant and slightly lower in energy than the latter.[18] The singlet-state reaction is, in general, expected to occur in the ^1L_a state. An MO calculation allowing for configuration interaction suggests that the increase in the reactivity of **1** upon photoexcitation is positionally dependent.[19] The reactivity sequences predicted by the free-valence index are 9>1>2 for the ^1L_a state and 9>2>1 for the ^1L_b state. If the ^1L_a state is active, photoaroylation would be expected to form three position isomers in yields following the same order as those of the reactivity sequences. However, the product distribution given was contrary to the theoretical expectation, appearring severly selective at the outer-ring positions.

The discrepancies between the theory and experiment may be partly explained by the steric effect. But this is not conclusive, since there is no reason why meso substitution should be predominant.

Third, these considerations result in the tentative conclusion that the exciplex is important in determining positional selectivity. It appears likely that the exciplex interaction leads to considerable changes in the electronic structure of ^{1}An*, resulting in a different enhancement of the chemical reactivity from that of the original molecule. Based on strong selectivity between the positions of the outer ring, it may be supposed that the electronic structure of ^{1}An* would change increasingly, particularly when the quencher approaches the outer ring. At this time, if the CT interaction occurs along the long axis of **1**, then it would cause greater stabilization of the longitudinally polarized ^1L_b state than of the transverse-polarized ^1L_a state.

The inversion of the electronic state is intramolecularly established in the aromatic compounds into which a powerful substituent is introduced. It is well-accepted that the substituent primarily shifts toward the red and intensifies an electronic transition band lying in the same direction as that of the extending conjugation.[18,20] In this connection, it should be noted that the absorption spectra of **3d** and **4d** are quite different from that of the parent **1**, while the absorption spectrum of **5d**

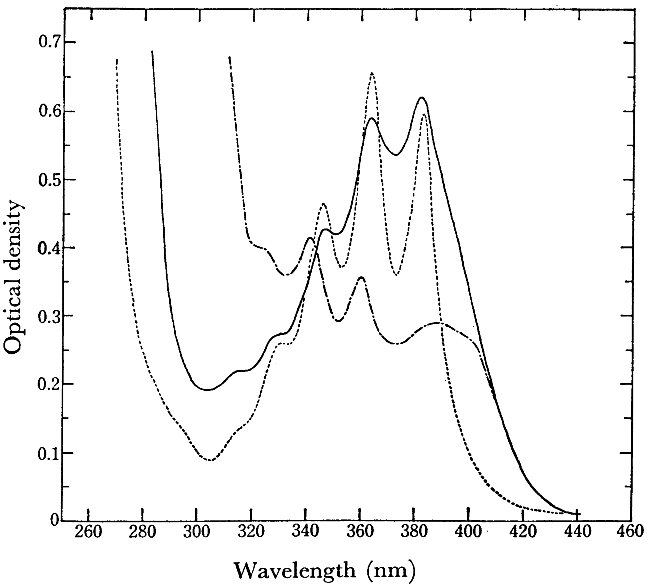

Fig. 5. Absorption spectra of 1-benzoylanthracene (solid line), 2-benzoylanthracene (broken line), and 9-benzoylanthracene (dotted line) in acetonitrile (10^{-4} M).

is similar in general shape and intensity to that of **1**, except for a slight shift to longer wavelengths, as is shown in Fig. 5. The spectral information implies that the electronic conjugation of the transition bands of the aromatic ring and benzoyl group is greatly enhanced when the substituent is introduced into the outer ring. The spectral deformation of 2-substituted **1** is known to be due to the result that the ^1L_b band emerges on the low-energy side of the ^1L_a band.[21] Such intramolecular interactions may be related to the intermolecular interaction of **1** with **2**.

Finally, ground-state complex formation will be considered. The Stern-Volmer treatment gave upward curvatures for **2h**—**j** with increasing concentration up to 2 M. This indicates that a contact complex is formed in the ground state,[22] although no change was observed in the absorption spectra, except for a slight red-shift due to the increasing dielectric constant of the solvent. A glassy ether solution containing **1** and **2g** or **h** at 77 K showed structureless fluorescence when excited at 390 nm. The corresponding absorption band was seen as a shoulder of the longest wavelength band of **1** in the excitation spectrum (Fig. 6). These spectra were confirmed to be different from those derived from anthracene aggregates,[23] since only the monomer bands were seen in the absence of the quencher. Therefore, the low-temperature emission is also indicative of the formation of CT complex related to that of the anthracene–trimesitinoyl chloride system reported by Briegleb.[24] Although very weak or no CT fluorescence was detected for the other aroyl chlorides, **2a**—**f**, which have less electron-withdrawing substituents, it appears likely that complex formation becomes feasible upon photo-excitation of the donor, since electronic excitation leads to a decrease in the ionic potential.[25]

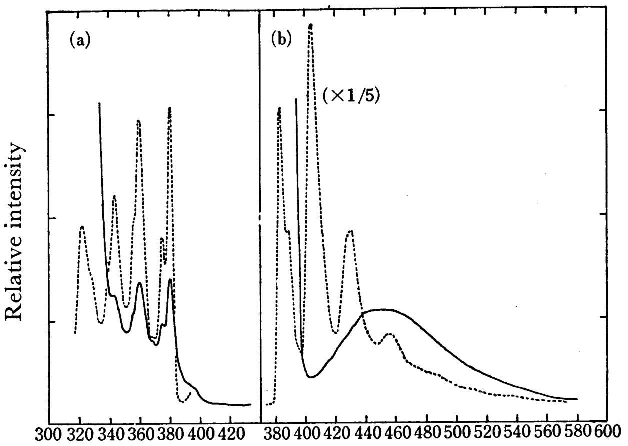

Fig. 6. Emission and excitation spectra of a mixture of anthracene (5×10^{-5} M) and *p*-chlorobenzoyl chloride (2 M) in a solid ether solution at 77 K: (a) excitation spectra for monitoring at 470 nm (solid line) and at 400 nm (dotted line); (b) emission spectra for excitation at 390 nm (solid line) and at 360 nm (broken line).

Experimental

Reagents. Benzoyl chloride was purified by washing with cold 5% aqueous sodium hydrogencarbonate followed by fractional distillation. The other aroyl chlorides available commercially or produced by ordinary procedures using the corresponding acids and thionyl chloride, were distilled twice *in vacuo* to eliminate hydrogen chloride. Anthracene was recrystallized three times from benzene. Benzene was washed with concentrated sulfuric acid and water, dried over calcium chloride, and then distilled over sodium. Acetonitrile was dried by shaking with silica gel and diphosphorus pentaoxide, and purified by fractional distillation over diphosphorus pentaoxide.

Irradiation. Benzene was used as the solvent in a series of preparative runs, since all the starting materials and products were largely soluble in it. The 365-nm light was isolated from a 500-W medium-pressure mercury lamp equipped with a filter combination composed of Corning 7-60 and Toshiba UV-35 filters and a cupric sulfonate solution. A reaction mixture (50 ml) of **1** (1×10^{-2} M in benzene and 3×10^{-3} M in acetonitrile) and **2** (0.1—0.13 M) in a Pyrex flask was exposed to the light in a nitrogen atmosphere at about 25 °C. Irradiation was carried out for 16 h. In most cases, the loss of **1** was about 60% of the starting quantities. In the cases of **2a**, **i**, and **j**, more prolonged irradiation periods (*ca.* 40 h) were required to accomplish the same conversion. After removal of the remaining **2** with aqueous sodium hydrogencarbonate and evaporation of the solvent, the products were subjected to chromatography on a silica column. Elution with a 4: 1 cyclohexane benzene solution gave two major and several minor products. The major products were characterized by their UV, IR, and NMR spectra, coloration with concentrated sulfulic acid, and emissive behavior in ethanol, as listed in Table 1. The anthracene dimer was obtained as a precipitate in the eluting solvent.

Irradiation using the 254-nm light was performed using an 8-W low-pressure mercury lamp without any filter. An acetonitrile solution (80 ml) of **1** (3×10^{-3} M) and **2d** (0.14 M) in a quartz flask was exposed to the light in nitrogen. The procedures for product isolation were the same as those noted above.

Photoreaction of 9-Benzoylanthracene. A benzene solution was exposed to a 500-W medium-pressure lamp. After irradiation, the solvent was evaporated and the residues were extracted with methanol to remove the remaining monomer. A white powder was obtained and was recrystallized from benzene. The product was identified as the dimer and decomposed at 217 °C to recover the monomer. It was also found that crystalline **5d** dispersed in water gave the dimer upon irradiation in air. Although it has been reported that crystalline **5d** undergoes autooxidation in the presence of light giving anthraquinone,26) no photooxidation was observed under the present conditions.

Quantum Yield Determinations. A low concentration of **1** (3×10^{-4} M) was employed to avoid photodimerization and to insure simple kinetics. At this concentration, the loss of **1** in the absence of the quencher was very small as compared with that in its presence. The amounts of **1** consumed in the presence of various concentrations of **2** (8×10^{-3}—3×10^{-2} M) were followed using a spectrophotometer at time intervals during the progress of the photoreaction and were subtracted from those in the absence of **2**. Since the photoproducts absorb increasing amounts of the incident light, resulting in a decrease in the photoreaction rate (see Fig. 1a), the quantum yields are based on the initial slopes of the conversion curves. Chemical changes in the dark were negligible. The incident and transmitted light intensities were monitored using potassium trioxalatoferrate(III) actinometry or an Eppley thermopile.

Errors were inevitable in determining the quantum yields. In the cases of **2i** and **j**, the conversion of **1** could not be precisely estimated, since the photoreaction rates were very slow under these conditions. A least-squares calculation was made to determine the values of the slope and the intercept in the plots of $1/\phi$ *vs.* $1/[\mathrm{Q}]$. The maximum error is ±30%.

Direct Photolysis of Aroyl Chlorides. Acetonitrile solutions of **2a**, **d**, and **h**—**j** (7—9×10^{-3} M) in quartz cells were exposed to an 8-W low-pressure lamp in nitrogen. The light intensity was determined using potassium trioxalatoferrate(III) actinometry. The aroyl chloride loss was estimated using the iron (III) hydroxamate method.27) The molar absorptivities (λ_{max}) of the iron(III) hydroxamates derived from the aroyl chlorides are as follows: 1.64×10^3 (550 nm) for **2a**, 1.47×10^3 (540 nm) for **2d**, 1.62×10^3 (530 nm) for **2h**, 1.54×10^3 (525 nm) for **2i**, and 1.61×10^3 (520 nm) for **2j**.

Fluorescence Measurements. The quenching measurements were made using a Hitachi MPF-2A spectrofluorometer at 20 °C. Samples were prepared in quartz cells constructed from 1-cm square tubing. The concentrations employed for **2** were in the same range as that for the quantum-yield determinations. Sample solutions containing **1** (10^{-4} M) and **2** were deoxygenated by purging with argon for 5 min before measurement. Since the unquenched spectral distribution was the same as that in the absence of the quencher, the relative fluorescence intensity was determined by estimating the height of the peak maximum. The quenching constant was calculated from the initial slope of the Stern-Volmer plots. The error is ±10%.

The emission and excitation spectra at 77 K were measured with a low-temperature cell compartment. The spectra are uncorrected. Upon careful cooling, a transparent solid glass solution was formed from an ether solution of **1** (5×10^{-5} M) and **2** (2 M), except for **2i** and **j**, for which measurements could not be made because of precipitation upon cooling resulting in cracks in the glassy solution. The emission measurements were made for excitation at 360 and 390 nm, for which the phosphorescence of **2** was negligible. On the other hand, the phosphorescence of **2** contributed largely to the shorter-wavelength side of the excitation spectra monitored at 470 nm, while only excitation spectra attributable to **1** were observed when monitored at 400 nm.

Preparation of the Authentic Compounds. 9-Benzoylanthracene **5d** was prepared according to the thermal Friedel-Crafts method using aluminum chloride as a catalyst.26) Mp 144—145 °C (lit,28) 148 °C)

Found: C, 90.08; H, 4.99%. Calcd for $C_{21}H_{14}O$: C, 89.23; H, 5.00%.

The other isomeric ketones, **3d** and **4d**, were prepared using the Grignard reaction of phenylmagnesium bromide with the corresponding cyanoanthracenes. To 4.4 g of 1-anthracenecarboxylic acid were added 3.6 g of *p*-toluenesulfonamide and 8.7 g of phosphorus pentachloride and the mixture was warmed in a hot-air bath. The temperature was gradually raised to 200 °C and the volatile products were distilled out. The cooled reaction mixture was treated with 8 ml of pyridine and gently warmed. To this solution was cautiously added 40 ml of water and the solid was collected. After washing with water and a 5% sodium hydroxide, the dried products were purified using silica-column chromatography with a benzene eluent. The 1-cyanoanthracene obtained was recrystallized from ethanol: yield, 90%; mp 142 °C (lit,29) 144.5 °C).

Found: C, 89.51; H, 4.33; N, 6.72%. Calcd for $C_{15}H_9N$; C, 88.64; H, 4.46; N, 6.89%.

2-Cyanoanthracene was prepared in a similar manner: yield, 95%; mp 195 °C (lit,29) 200 °C).

Found: C, 88.44; H, 4.28; N, 6.79%.

To 0.3 g of cyanoanthracene in 20 ml of benzene was added an equimolar amount of phenyl magnesium bromide in ether. The reaction mixture was warmed and ether was distilled out. The residual benzene solution was refluxed for 2 h. After treatment with ammonium chloride, the ketimine was extracted with aqueous acetic acid (1:1) and hydrolyzed under reflux for 1 h. The addition of a mineral acid, such as hydrogen chloride, was important for hydrolysis of the *l*-isomer. Yellow products were extracted with benzene and purified by silica-column chromatography. Elution with benzene gave the corresponding ketones.

1-Benzoylanthracene **3d**: yield, 58%; mp 138—139 °C (lit,29) 141 °C).

Found: C, 89.52; H, 5.04%.

2-Benzoylanthracene **4d**: yield, 86%, mp 178 °C (lit,29) 175 °C)

Found: C, 90.07, H, 4.95%.

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