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Studies on Chemiluminescent Compounds. I. Syntheses of Acyl-substituted Anthracene Derivatives and Their Chemiluminescence

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New anthracene derivatives with a –COCH– group, such as 1,5-dipropionylanthracene, 1,8-dipropionylanthracene, 1,5-di-isobutyrylanthracene, 1,8-diisobutyrylanthracene, 1,5-bis[3-(methoxycarbonyl)propionyl]-anthracene, 1,8-bis[3-(methoxycarbonyl)propionyl]anthracene, 1,5-bis(cyclohexylcarbonyl)anthracene, 3,7-diisopropyl-1,5-diisobutyrylanthracene, and 5-dimethylamino-4-isobutyryl-1-methoxyanthracene (**10**) have been synthesized. Their direct chemiluminescences were studied by air oxidation in alkaline solutions. The properties of the chemiluminescence have been found to be influenced by not only the class of the C–H bond adjacent to the carbonyl group but also by the electronic properties of the aromatic ring system, the solvent, and the additive. **10** exhibited the longest chemiluminescence. This chemiluminescent phenomenon might be explained by a chemically initiated electron exchange luminescence (CIEEL) mechanism.

Since luminescence is an emission from an electronic excited state, the necessary excited molecule must be produced in any chemiluminescent reaction. Recent investigations suggest that effective excited molecules (singlet state) are produced in decomposition reactions of cyclic peroxides such as 1,2-dioxetanes, and 1,2-dioxetanones.[1) These intermediate peroxides are thought to exist also in bioluminescence. Most of the bioluminescence processes are remarkably efficient and show direct luminescence from the air oxidation of luciferins. The quantum yield for an enzymatic process as in a firefly is approximately 0.88 einstein mol^{-1}.[2)

Kamiya and Sugimoto studied indirect chemiluminescence: the transfer of energy from activated carbonyl intermediates in the oxidation of compounds having –COCH– groups to 9,10-dibromoanthracene or 9,10-diphenylanthracene. They observed strong luminescence when the C–H bond adjacent to the carbonyl group is tertiary C–H. They also reported that 4-hydroxy or 4-methoxy-substituted aromatic ketones gave effective singlet excited states. They did not, however, mention the effect of the catalyst and the additives on the chemiluminescence of the compounds mentioned above.[3) They recently reported the direct chemiluminescence of 9,10-diisobutyrylanthracene in the alkaline air oxidation, but they did not mention the effects of substitution in the anthracene ring, of basicity of the catalyst, and of the additives.[3)

In the practical use of chemiluminescence, the radiation of light of 500—520 nm is preferred because of strong human sensitivity to light in this region. Direct chemiluminescence in the benzene system fails to produce visible radiation of such a long wave length. But the use of anthracene compounds makes it possible to radiate the light of 500 nm and to make a practical light source for human beings. The lack of the investigation of details in the mechanism of chemiluminescence of anthracene type ketones motivated our present work.

We report in this paper the effects of substitution in anthracene ring, of basicity of catalyst, and of the additives, with the hope of the development of light for practical use.

To investigate the direct chemiluminescence mechanism, anthracene compounds **1**—**10** were synthesized and examined in various alkali catalyst oxidations with additives such as crown ether. We will discuss the chemiluminescence mechanism based on the observed chemiluminescence spectra. We suggest that an excited singlet state carbonyl may be generated by the air oxidation of these anthracenes. The mechanism is explained in terms of chemically initiated electron exchange luminescence (CIEEL).[4)

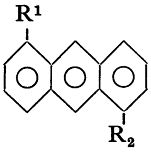
Results and Discussion

In order to investigate the substituent effects on the direct chemiluminescence from the air oxidation of anthracene derivatives, we newly synthesized several compounds listed in Tables 1, 2, and 3 using the usual Friedel-Crafts acylation.[5)

Reaction of Acyl Chloride with Anthracenes. The reaction of anthracene derivatives with several acyl chlorides and anhydrous aluminum chloride in anhydrous carbon disulfide afforded the corresponding compounds **1**—**10**. In most cases, carbonyl groups are introduced at the 1-position or at both 1 and 5-positions of anthracene.[6) However, in the reaction of anthracene with isobutyryl chloride, alkylation reaction also occurred in part to afford 3,7-diisopropyl-1,5-diisobutyrylanthracene (**9**). The reaction of isopropyl chloride with 1,5-diisobutyrylanthracene (**3**) in the presence of excess anhydrous aluminum chloride gave the same alkylated diketone **9**. A similar alkylation in the Friedel-Crafts acylation reaction has been reported by Rothstein and Saville.[7) They suggested that alkylation took place *via* the decarbonylated acyl chloride-aluminum chloride addition complex ($R^+ \cdot AlCl_4^-$) when less reactive aromatic compounds were used. Compound **9** might be produced in the same manner. Anthracene and more reactive anthracene derivatives such as 1-dimethylamino-5-methoxyanthracene were easily acylated. The acylation of 1,5-diisobutyrylanthracene did not proceed. The reaction gave only a dialkyl diacyl derivative. This might be due to the deactivation by two carbonyl groups.

Chemiluminescence in the Air Oxidation of Anthracenes. The direct chemiluminescence was observed upon adding potassium *t*-butoxide (^{t}BuOK) in *t*-butyl alcohol or potassium hydroxide (KOH) in water to these ketones in various aerated solvents, such as

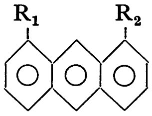
Table 1. The chemiluminescence with 1,5-disubstituted anthracenes by air oxidation[a]



R_1, R_2		Base	Life time / min	Light emission	Colors of resulting solns
$COCH_3$	(**1**)	^{t}BuOK or KOH	≈0	none	dark purple (in DMSO)
$COCH_2CH_3$	(**2**)	^{t}BuOK or KOH	≈0	very weak	dark purple (in DMSO or DBP)
$COCH(CH_3)_2$	(**3**)	^{t}BuOK or KOH	≈0.5	medium	dark orange (in DMSO or DBP)
COC_6H_{11}	(**4**)	^{t}BuOK	≈0.5	medium	dark orange (in DMSO)
$COCH_2CH_2CO_2Me$	(**5**)	^{t}BuOKor KOH	≈0.5	weak	dark purple (in DMSO)

a) A solution of ^{t}BuOK (0.35 mmol) in *t*-butyl alcohol (1 ml) was added to a stirred solution of anthracenes (0.001 mmol) in dimethyl sulfoxide (1 ml) or dibutyl phthalate (1 ml) at 25 °C or a solution of KOH (0.35 mmol) in H_2O (0.1 ml) was added to a stirred solution of anthracenes (0.001 mmol) in dimethyl sulfoxide (1.9 ml) or dibutyl phthalate (1.9 ml) at 25 °C.

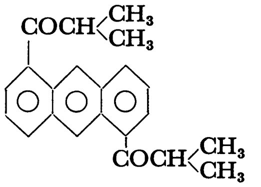
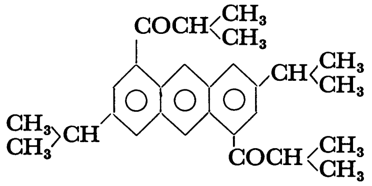
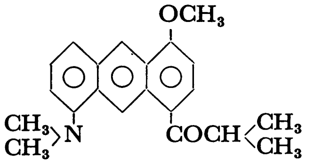
Table 2. The chemiluminescence with 1,8-disubstituted anthracenes by air oxidation[a]



R_1, R_2		Base	Life time / min	Light emission	Colors of resulting solns
$COCH_2CH_3$	(**6**)	^{t}BuOK or KOH	≈0	very weak	dark purple (in DMSO)
$COCH(CH_3)_2$	(**7**)	^{t}BuOK or KOH	≈0.5	weak	dark orange (in DMSO)
$COCH_2CH_2CO_2Me$	(**8**)	^{t}BuOK	≈0	very weak	dark orange (in DBP)

a) Table 1 footnote a).

Table 3. The chemiluminescence with 1,5-disubstituted anthracenes by air oxidation[a]

Compd		Base	Life time / min	Light emission	Colors of resulting solns
	(**3**)	^{t}BuOK or KOH	≈0.5	medium	dark orange (in DMSO orDBP)
	(**9**)	^{t}BuOK or KOH	≈1	very strong	orange (in DMSO)
	(**14**)	^{t}BuOK	≈30	very strong	greenish yellow (in DMSO)

a) Table 1 footnote a).

dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), benzene, or phthalic esters. The chemiluminescent responses were changed by the experimental conditions—*i.e.* by the solvent, by the concentrations of ketones and catalysts, more essentially by the electronic properties of the aromatic ring systems, and by the chemical structures of the ketones. The properties of chemiluminescence examined in DMSO or dibutyl phthalate (DBP) solution, using ^{t}BuOK or KOH as a base, are listed in Tables 1, 2, and 3 for 1,5-disubstituted, 1,8-disubstituted, and multi-substituted anthracenes, respectively, together with the colors of the resulting solutions. The results in the tables show that the efficiency of the emission is influenced both by the class of the C–H bond adjacent to the carbonyl group and by the electronic properties of the aromatic ring systems. The former was discussed by Kamiya *et al.*, who showed that a compound possessing a C–H bond adjacent to carbonyl group gave the most intensive chemiluminescence.3) Our results showed the similar behavior of the chemiluminescent reaction. From Table 3, it can be seen that electron-donating groups such as dimethylamino or methoxy groups strongly increase quantum yield and lengthen chemiluminescence time. Thus, 5-dimethylamino-4-isobutyryl-1-methoxyanthracene (**10**) exhibits the most intensive and longest chemiluminescence among all of these ketones.

We also examined the fluorescence and chemiluminescence spectra of ketones **3**, **9**, and **10**, which are shown in Figs. 1, 2, and 3. In Figs. 1 and 2, the chemiluminescent spectra of the ketones **3** and **9** are red-shifted compared to those of the two air-oxidated products. Contrary to this, in Fig. 3, the chemiluminescent spectrum of ketone **10** shows a pattern closely similar to the fluorescent spectrum of the methyl ester of its air-oxidated product. The final products of the air oxidation of these ketones were the corresponding acids.

In order to obtain the best conditions for the chemi-

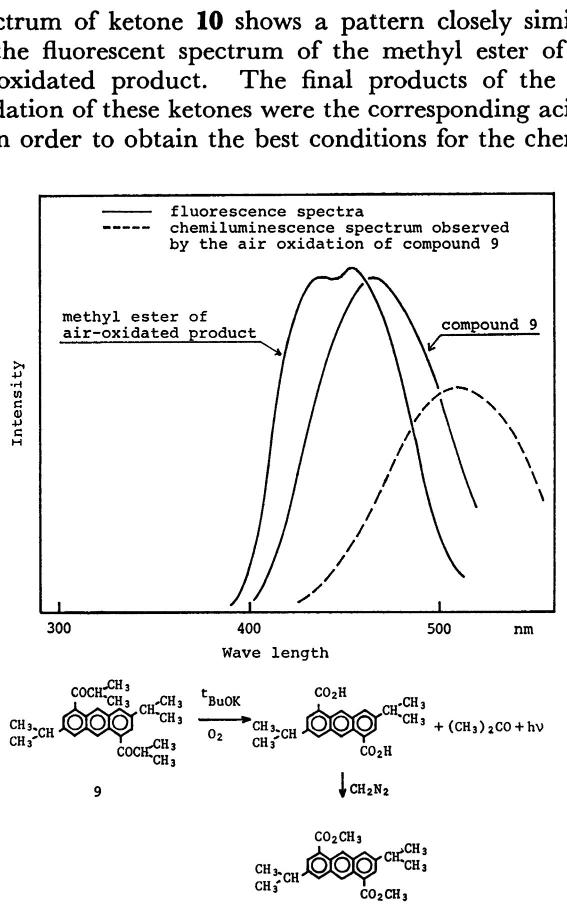


Fig. 2. Fluorescence and chemiluminescence spectra of 3,7-diisopropyl-1,5-diisobutyrylanthracene (**9**) and its oxidated product.

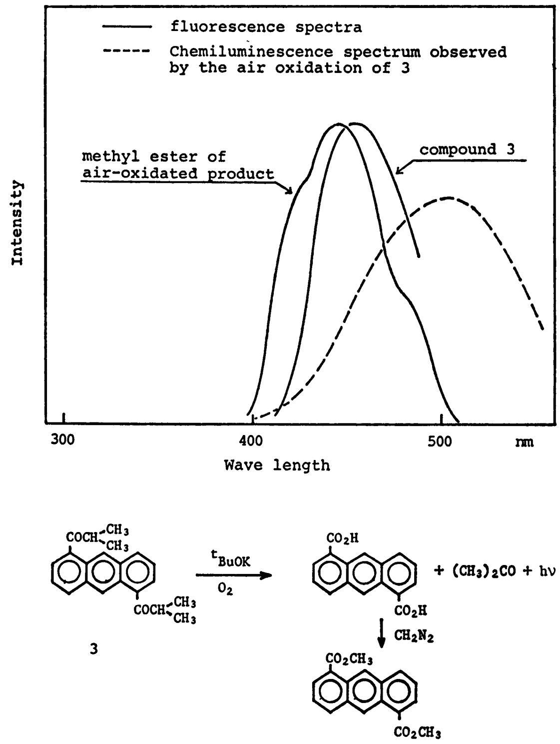


Fig. 1. Fluorescence and chemiluminescence spectra of 1,5-diisobutyrylanthracene (**3**) and its oxidated product.

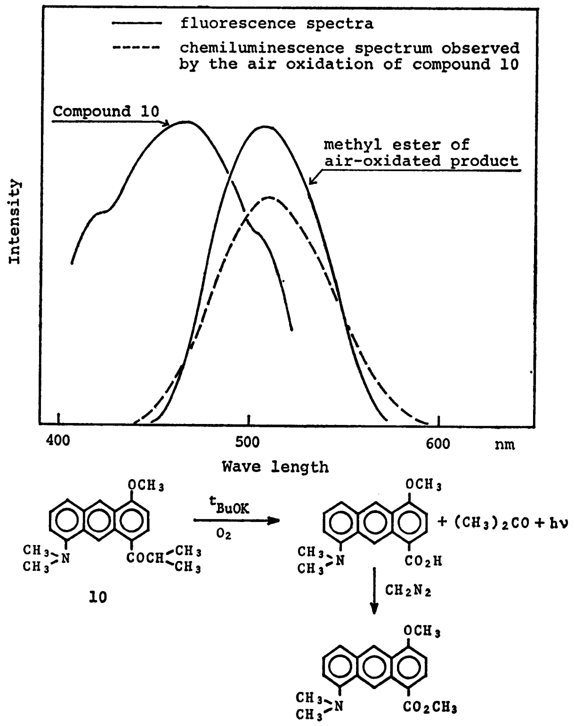


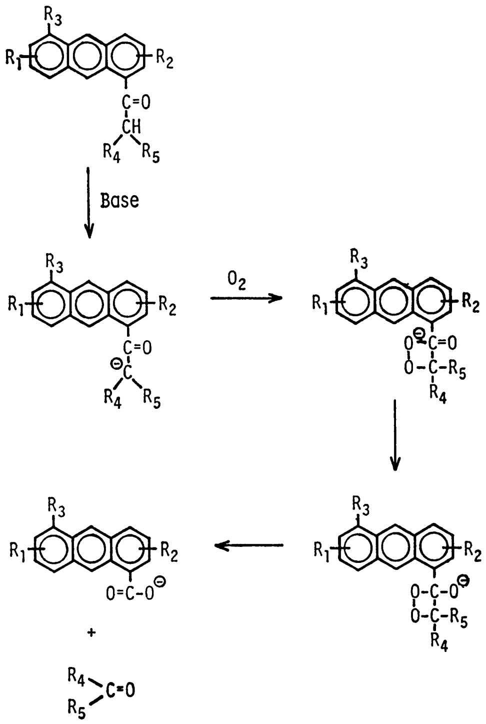
Fig. 3. Fluorescence and chemiluminescence spectra of 5-dimethylamino-4-isobutyryl-1-methoxyanthracene (**10**) and its oxidated product.

TABLE 4. THE EFFECTS OF BASE AND ADDITIVE (DICYCLOHEXANO-18-CROWN-6(C.E.)) ON THE EFFICIENCY OF EMISSION OF COMPOUND **10**

Condition	1[e]	2[e]	3[e]	4[f]
Base and additive	^{t}BuOK/^{t}BuOH	^{t}BuORb/^{t}BuOH	^{t}BuOCs/^{t}BuOH	^{t}BuOK+ C.E.
$i_{\max}$[a]	1.00	0.61	0.88	46.0
$t_{\max}$[b]	10 min	20 min	11 min	0.5 min
$t_{1/4}$[c]	81 min	110 min	75 min	1.0 min
Quantum yield[d]	2.5%	2.0%	2.0%	4.6%

a) The relative intensity of the emission peaks; the intensity of the emission peak under conditions 1 was defined as 1.00. b) The time needed for the intensity of the emission to reach a maximum. c) The time for the intensity to decay to one-fourth of the maximum value. d) These were measured in benzene solution at 25 °C. e) To a stirred solution of compound **10** (0.002 mmol) in benzene (1 ml) was added a solution of ^{t}BuOM (0.35 mmol) in ^{t}BuOH (1 ml). f) To a stirred mixture of compound **10** (0.002 mmol), benzene (1.9 ml), and powdered ^{t}BuOK (40 mg) was added dicyclohexano-18-crown-6 (0.2 mmol).

luminescent reaction, we investigated the effects of solvent, of base, and of additives, using ketone **10**, which has the longest chemiluminescence. Nonpolar solvents such as benzene, toluene and xylene extended the life-time of the emission. The effects of the base and the additive are summarized in Table 4. When benzene was used as a solvent, the addition of dicyclohexano-18-crown-6 as an additive was the most effective: the quantum yield of chemiluminescence reached 0.046 einstein mol^{-1}. This value is approximately three-times as high as those produced using the Seliger-Lee luminol standard.[8] These results suggest that intermediate dioxetane species which will be generated by the oxygenation of the anion of ketones are formed as described in the following mechanism:



Conclusion

The efficiency of chemiluminescence increases when an electron-donating group is attached to the aromatic ring (**10**) and the chemiluminescent spectrum of ketone **10** shows a pattern closely similar to the fluorescent spectrum of its air-oxidated product. These findings suggest that this chemiluminescence may be generated *via* CIEEL mechanism. By contrast, the emission from ketones **3** and **9** may be generated from the intermediate intramolecular exciplex, because the chemiluminescent spectra are red-shifted compared to those of the air-oxidated products.

Werner *et al.* reported that, for anthracenes in general, the energy of the first excited singlet state (S_1) is observed to decrease as solvent polarity increases.[9] We think that the low efficiency of chemiluminescence in polar solvents is due to the efficient intersystem crossing from S_1 to T_1. Dicyclohexano-18-crown-6 may play an important role in dissolving the catalyst in a nonpolar solvent.

In summary, we have synthesized several anthracene derivatives which showed chemiluminescence by air-oxidation, using a base as a catalyst. 5-Dimethylamino-4-isobutyryl-1-methoxyanthracene (**10**) exhibits the most intensive chemiluminescence. This may be generated *via* CIEEL mechanism.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were run on a JEOL-MH-100 NMR spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. ^{13}C NMR spectra were taken on a JEOL-FT-NMR spectrometer FX200 apparatus, using $CDCl_3$ as solvent and tetramethylsilane as an internal reference. Infrared spectra were recorded on Shimadzu IR-400 spectrometer as Nujol mulls. Mass spectra were determined on a JEOL-JMS-D-100. Chemiluminescence spectra were measured using a Shimadzu spectrofluorophotometer RF-520 and are uncorrected. Column chromatography was carried out using Wako silica gel C-200 with cyclohexane–benzene mixture from 1 : 0.1—1 : 3 or benzene as an eluent. The solvents for the column chromatography were obtained from Tokyo Kasei Co., Ltd. and were used without purification.

General Procedure for Friedel-Crafts Acylation of Anthracenes with Acyl Chlorides. A solution of anhydrous aluminum chloride (0.06 mol) and the acyl chloride (0.06 mol) in 30 ml of anhydrous carbon disulfide was added to a stirred solution of anthracene (3.6 g, 0.02 mol) in 35 ml anhydrous carbon disulfide at 20—25 °C and the mixture was stirred for 2—5 h at room temperature or at reflux. The reaction mixture was poured to a 200 ml beaker nearly filled with a mixture of crushed ice and concentrated hydrochloric acid. The organic layer was extracted with benzene, washed with 5% aqueous sodium hydrogencarbonate solution, and evaporated to dryness. Isolation and purification of each product were performed with column chromatography on silica gel.

Analyses and properties of the products are described below. Specific examples of the acylation are given in detail below.

1,5-Dipropionylanthracene (2): Yield 28%; mp 169—171.5 °C; IR 1675 cm^{-1}; NMR ($CDCl_3$): δ=1.32 (6H, t, J=9.0 Hz), 3.12 (4H, q, J=9.0 Hz), 7.45 (2H, dd, J=7.0 and 8.0

Hz), 7.96 (2H, d, J=7.0 Hz), 8.20 (2H, d, J=8.0 Hz), and 9.40 (2H, s). MS *m/e*: 290. Found: C, 82.70; H, 6.23%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

1,8-Dipropionylanthracene (6): Yield 13%; mp 169—171.5 °C; IR 1675 cm^{-1}; NMR ($CDCl_3$): δ=1.30 (6H, t, J=7.5 Hz), 3.08 (4H, q, J=7.5 Hz), 7.40 (2H, dd, J=7.0 and 7.5 Hz), 7.75 (2H, d, J=7.0 Hz), 8.04 (2H, d, J=7.5 Hz), 8.36 (1H, s), and 9.77 (1H, s). MS *m/e*: 290. Found: C, 82.91; H, 6.24%. Calcd for $C_{20}H_{18}O_2$: C, 82.73, H, 6.25%.

1,5-Bis(cyclohexylcarbonyl)anthracene (4): Yield 37%; mp 208—210 °C; IR 1690 cm^{-1}; NMR ($CDCl_3$): δ=1.20—2.10 (20H, m), 3.10—3.50 (2H, m), 7.46 (2H, dd, J=7.0 and 8.5 Hz), 7.86 (2H, d, J=7.0 Hz), 8.16 (2H, d, J=8.5 Hz), and 9.06 (2H, s). MS *m/e*: 398. Found: C, 84.26; H, 7.62%. Calcd for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59%.

1,5-Bis[3-(methoxycarbonyl)propionyl]anthracene (5): Yield 23%; IR 1735 cm^{-1}; NMR ($CDCl_3$): δ=2.88 (4H, t, J=6.0 Hz), 3.48 (4H, t, J=6.0 Hz), 3.76 (6H, s), 7.52 (2H, dd, J=7.0 and 8.5 Hz), 8.12 (2H, d, J=7.0 Hz), 8.26 (2H, d, J=8.5 Hz), and 9.45 (2H, s). MS *m/e*: Found: C, 71.20; H, 5.32%. Calcd for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46%.

1,8-Bis[3-(methoxycarbonyl)propionyl]anthracene (8): Yield 11%; mp 172.5—175 °C; IR 1730—1745 cm^{-1}; NMR ($CDCl_3$): δ=2.92 (4H, t, J=7.0 Hz), 3.45 (4H, t, J=7.0 Hz), 3.76 (6H, s), 7.45 (2H, dd, J=7.0 and 8.0 Hz), 8.02 (2H, d, J=7.0 Hz), 8.18 (2H, d, J=8.0 Hz), 8.50 (1H, s), and 9.92 (1H, s). MS *m/e*: 406. Found: C, 70.98; H, 5.42%. Calcd for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46%.

Reaction of Anthracene with Isobutyryl Chloride. A solution of aluminum chloride (8.0 g) and isobutyryl chloride (6.4 g) in 30 ml of anhydrous carbon disulfide was added to a stirred solution of anthracene (3.6 g) in 35 ml anhydrous carbon disulfide at 20 °C and the mixture was stirred for 5 h at reflux. The reaction mixture was poured into a 200 ml beaker nearly filled with a mixture of ice and concentrated hydrochloric acid. The organic substances were extracted with benzene and washed with 5% aqueous sodium hydrogencarbonate. Then the solvent was evaporated to dryness. The obtained residue was subjected to column chromatography with benzene as an eluent. The crude crystalline products were separated and recrystallized from ethanol to afford three pure products:

1,5-Diisobutyrylanthracene (3): Yield 2.16 g (34%). Mp 124.5—126 °C; IR 1675 cm^{-1}; NMR ($CDCl_3$): δ=1.28 (12H, d, J=8.0 Hz), 3.69 (2H, sept, J=8.0 Hz), 7.44 (2H, dd, J=7.0 and 8.0 Hz), 7.83 (2H, d, J=7.0 Hz), 8.14 (2H, d, J=8.0 Hz), and 9.08 (2H, s). ^{13}C-NMR ($CDCl_3$): δ=18.9, 39.0, 124.1, 126.0, 127.5, 128.3, 133.0, 133.5, 135.5, and 208.2 Hz. MS *m/e*: 318. Found: C, 83.10; H, 6.88%. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96%.

1,8-Diisobutyrylanthracene (7): Yield 0.75 g (12%). Mp 102.5—104.5 °C; IR 1675 cm^{-1}; NMR ($CDCl_3$): δ=1.28 (12H, d, J=8.0 Hz), 3.54 (2H, sept. J=8.0 Hz), 7.43 (2H, dd, J=7.0 and 8.0 Hz), 7.67 (2H, d, J=7.0 Hz), 8.04 (2H, d, J=8.0 Hz), 8.40 (1H, s), and 9.18 (1H, s). MS *m/e*: 318. Found: C, 82.73; H, 6.99%. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96%.

3,7-Diisopropyl-1,5-diisobutyrylanthracene (9): Yield 0.12 g (1.5%). Mp 192—195 °C; IR 1680 cm^{-1}; NMR ($CDCl_3$): δ=1.27 (12H, d, J=8.0 Hz), 1.40 (12H, d, J=8.0 Hz), 3.08 (2H, sept, J=8.0 Hz), 3.56 (2H, sept, J=8.0 Hz), 7.65 (2H, s), 7.90 (2H, s), and 8.91 (2H, s). ^{13}C-NMR ($CDCl_3$): δ=19.0, 23.5 34.1, 39.1, 125.0, 127.5, 128.1 128.2, 132.9, 135.7, 143.8, and 208.5 Hz. MS *m/e*: 402. Found: C, 83.38; H, 8.44%. Calcd for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51%.

Reaction of 1,5-Diisobutyrylanthracene with Isobutyryl Chloride. To a stirred mixture of 1,5-diisobutyrylanthracene (4.8 g) and aluminum chloride (16 g) in anhydrous carbon disulfide (20 ml) was added a solution of isobutyryl chloride (8.0 g) in anhydrous carbon disulfide (5 ml) at 20 °C. The mixture was stirred overnight and treated as described above. Separation by column chromatography and recrystallization from ethanol–hexane afforded 3,7-diisopropyl-1,5-diisobutyrylanthracene (**9**): Yield 1.05 g (17.4%).

Reaction of 1-Isobutyrylanthracene with Isobutyryl Chloride. To a stirred mixture of 1-isobutyrylanthracene (2.5 g) and aluminum chloride (10.7 g) in anhydrous carbon disulfide (20 ml) was added a solution of isobutyryl chloride (8.5 g) in anhydrous carbon disulfide (5 ml) at 25 °C. The mixture was stirred overnight at 25 °C and treated as described above. Separation using column chromatography and recrystallization from ethanol–hexane afforded 1,5-diisobutyrylanthracene (**3**) (0.36 g, 11%), and 3,7-diisopropyl-1,5-diisobutyrylanthracene (**9**) (0.4 g, 10%).

Reaction of 1,5-Diisobutyrylanthracene with Isopropyl Chloride. To a stirred mixture of 1,5-diisobutyrylanthracene (1.6 g) and aluminum chloride (6.7 g) in anhydrous carbon disulfide (20 ml) was added a solution of isopropyl chloride (4.0 g) in anhydrous carbon disulfide (10 ml) at 25 °C. The mixture was stirred at 25 °C for 6 h, then for 2 d at reflux, and treated as described above. The starting 1.5-diisobutyrylanthracene was recovered (1.1 g) and 3.7-diisopropyl-1,5-diisobutyrylanthracene (**9**) (0.4 g, 19.4%) was separated out.

Reaction of 1-Dimethylamino-5-methoxyanthracene with Isobutyryl Chloride. A solution of anhydrous aluminum chloride (0.06 mol) and isobutyryl chloride (0.06 mol) in 30 ml of anhydrous carbon disulfide was added to a stirred mixture of 1-dimethylamino-5-methoxyanthracene (5.0 g, 0.02 mol) in 30 ml anhydrous carbon disulfide at 0—5 °C. The mixture was stirred at the same temperature for 3 h. The reaction mixture was treated as described above. Isolation and purification gave a greenish crystalline material identified as 5-dimethylamino-4-isobutyryl-1-methoxyanthracene; Yield 2.0 g (31.2%). Mp 134.5—139 °C; IR 1675 cm^{-1}; NMR ($CDCl_3$): δ=1.30 (6H, d, J=6.0 Hz), 3.00 (6H, s), 3.66 (1H, sept, J=6.0 Hz), 4.12 (3H, s), 6.66 (1H, d, J=8.5 Hz), 6.98 (1H, d, J=8.0 Hz), 7.38 (1H, dd, J=8.0 and 9.0 Hz), 7.66 (1H, d, J=9.0 Hz), 7.86 (1H, d, J=8.5 Hz), 8.80 (1H, s), and 9.58 (1H, s). MS *m/e*: 321. Found: C, 78.27; H, 7.10; N, 4.56%. Calcd for $C_{21}H_{23}O_2N$: C, 78.47; H, 7.21; N, 4.36%.

The Measurement of Chemiluminescence. Commercially available KOH (from Kanto Chemical Co., Inc.), and ^{t}BuOK (from Merck for synthesis) were used without further purification. Other alkali metal *t*-butoxides were prepared by dissolving an alkali metal in *t*-butyl alcohol. Luminol was recrystallized from dilute hydrochloric acid prior to use. All solvents used were purified by distillation. The luminescent reaction was initiated by adding a base to an aerated solution of ketone, with stirring, in a quartz cell (10×10×45 mm) which was situated in a thermostatically-controlled cell holder. The chemiluminescent intensity was measured on a Shimazu spectrofluorophotometer RF-520 with no exciting source. The total light emission was determined graphically from the *I-t* curves. A standard solution of luminol in anhydrous DMSO having an optical density at 359.5 nm (the absorption peak) of 0.010 (1.26×10^{-6} mol l^{-1}) was prepared, and the *I-t* curve of the chemiluminescence initiated by adding 0.2 ml of a ^{t}BuOK solution to 2 ml of the standard solution was measured on the same apparatus at 313 K. Using the value of 1.28×10^{-2} einstein mol^{-1} proposed by Lee *et al.* for the chemiluminescence exhibited from the luminol solution, the quantum yields for direct chemiluminescence from ketones were determined from the ratio of the total light emitted from the luminol solutionto the total measured light emission from the ketone solutions.

*Methyl Ester of the Air-oxidated Product of Compound **3**, **9**, and **10**.* To a stirred solution of compound **3**, **9**, or **10** in benzene was added a solution of excess amount of potassium *t*-butoxide in *t*-butyl alcohol at 20 °C. Then chemiluminescence was observed. Water was added to the resulting mixture and stirred vigorously. The aqueous layer was separated, neutralized with acetic acid and extracted with chloroform. To this organic solution was added a solution of diazomethane in ethyl ether. After stirring for 1 h, the solvent was evaporated to dryness. The obtained residue was subjetced to column chromatography with benzene as an eluent. The methyl ester of compound **3**, **9**, or **10** was obtained.

1,5-Bis(methoxycarbonyl)anthracene: Mp 123—125 °C; IR 1710 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$): δ=4.06 (6H, s), 7.54 (2H, t, J=8.0 Hz), 8.30 (4H, d, J=8.0 Hz), and 9.65 (2H, s). Found: C, 73.63; H, 4.53%. Calcd for $\mathrm{C_{18}H_{14}O_4}$: C, 73.46; H, 4.80%.

3,7-Diisopropyl-1,5-bis(methoxycarbonyl)anthracene: Mp 149—151 °C; IR 1705 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$): δ=1.38 (12H, d, J=8.0 Hz), 3.10 (2H, sept, J=8.0 Hz), 4.02 (6H, s), 8.00 (2H, s), 8.12 (2H, s), and 9.40 (2H, s). Found: C, 75.80; H, 7.02%. Calcd for $\mathrm{C_{24}H_{26}O_4}$: C, 76.16; H, 6.93%.

5-Dimethylamino-1-methoxy-4-(methoxycarbonyl)anthracene: Mp 130—131 °C; IR 1700 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$): δ=3.00 (6H, s), 3.96 (3H, s), 4.00 (3H, s), 6.58 (1H, d, J=8.0 Hz), 6.92 (1H, d, J=8.0 Hz), 7.32 (1H, t, J=8.0 Hz), 7.58 (1H, d, J=8.0 Hz), 8.14 (1H, d, J=8.0 Hz), 8.74 (1H, s), and 9.92 (1H, s). Found: C, 74.00; H, 6.02; N, 4.62%. Calcd for $\mathrm{C_{19}H_{19}O_3N}$: C, 73.76; H, 6.19; N, 4.53%.

References

1) F. McCapra, *J. Chem. Soc., Chem. Commun.*, **1977**, 946; M. J. S. Dewar and L. Kirschner, *J. Am. Chem. Soc.*, **96**, 7578 (1974); D. R. Roberts, *J. Chem. Soc., Chem. Commun.*, **1974**, 683; G. Barnett, *Can. J. Chem.*, **52**, 3837 (1974); N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **95**, 264 (1973); M. A. Umbreit and E. H. White, *J. Org. Chem.*, **41**, 479 (1976); K. R. Kopecky J. E. Filby, C. Mumford, P. A. Lockwood, and J. Y. Ding, *Can. J. Chem.*, **53**, 1103 (1975).

2) H. H. Seliger and W. D. McElroy, *Biochem. Biophys. Res. Commun.*, **1**, 21 (1959); H. H. Seliger and W. D. McElroy *Arch. Biochem. Biophys.*, **88**, 136 (1960).

3) I. Kamiya and K. Aoki, *Bull. Chem. Soc. Jpn.*, **47**, 1744 (1974); I. Kamiya and T. Sugimoto, *Chem. Lett.*, **1976**, 33; I. Kamiya and T. Susimoto *Bull. Chem. Soc. Jpn.*, **50**, 2442 (1977); I. Kamiya and T. Sugimoto *Chem. Lett.*, **1978**, 335.

4) J. Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 6107 (1977); **100**, 4496 (1978); F. McCapra, *J. Chem. Soc., Chem. Commun.*, **1977**, 946; K. A. Zaklika, A. L. Thayer, and A.P. Schaap, *J. Am. Chem. Soc.*, **100**, 4916 (1978); K. A. Zaklika, P. A. Burns, and A. P. Schaap, *ibid.*, **100**, 318 (1978).

5) "Friedel-Crafts and Related Reactions," ed by G.A. Olah, Interscience, New York, N. Y. (1964), Vol. III, Part 1.

6) P. H. Gore and C. K. Thadani, *J. Chem. Soc.*, *C*, **1966**, 1729.

7) E. Rothstein and R. W. Waville, *J. Chem. Soc.*, **1949**, 1961.

8) J. Lee, A. S. Wesley, J. F. Ferguson, and H. H. Seliger, "Bioluminescence in Progress," ed by F. H. Johnson and Y. Haneda, Princeton University Press, New Jersey (1966), p. 35.

9) T. C. Werner, T. Matthews, and B. Soller, *J. Phys. Chem.*, **77**, 1611 (1973).