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Amide Ion Formation and *N*-Alkylation of Aminoanthraquinones in the Presence of Potassium Hydroxide in Dimethyl Sulfoxide1)

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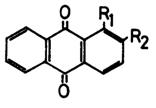
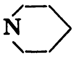
Amide ions were formed by the deprotonation of the amino group of amino- and (monoalkylamino)-anthraquinones in the presence of powdered potassium hydroxide in dimethyl sulfoxide (DMSO). Under a nitrogen atmosphere these amide ions changed to their radical anions. The amide ions of 1-aminoanthraquinones reacted with excess alkyl halides to yield 1-alkylaminoanthraquinones, while the *N*-alkylation of 2-aminoanthraquinones afforded 2-dialkylaminoanthraquinones in good yields. 2-Aminobenzophenone underwent mono-*N*-alkylation, while 4-aminoazobenzene and p-nitroaniline underwent di-*N*-alkylation. It was also found that the carbanion of DMSO easily attacked the carbonyl group of the (dialkylamino)-anthraquinones.

During the course of our studies on the photonucleophilic reactions2) we examined a reaction between an hydroxide ion and aminoanthraquinones. We found that the color of the aminoanthraquinones rapidly changed from red or orange to green upon being mixed with powdered potassium hydroxide (KOH) in dipolar aprotic solvents such as dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and pyridine. The color changes of aminoanthraquinones caused by the action of alkali hydroxide have attracted attention for a long time in relation to the mechanism of indanthrone formation by the fusion of 2-aminoanthraquinone with KOH.3–5) However, no decisive evidence regarding the mechanism of the color reactions has been presented, and the behavior of aminoanthraquinones in an alkaline media still remains obscure.

In this paper we describe in detail the behavior of aminoanthraquinones in an KOH–DMSO system under air and nitrogen atmosphere. It also describes how aminoanthraquinones and some aromatic amines having an electron-withdrawing group are easily *N*-alkylated by alkyl halides *via* their amide ions in the presence of powdered KOH in DMSO.



	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
R_1	NH_2	$NHCH_3$	$N(CH_3)_2$		H	H	H	H
R_2	H	H	H	H	NH_2	NHC_4H_9	$N(C_4H_9)_2$	

Results and Discussion

The Formation of Amide Ion. When 1-aminoanthraquinone(**1**) was mixed with powdered KOH6) in DMSO at room temperature, the solution turned from orange to green. The visible absorption spectra of a **1**–KOH–DMSO system are shown in Fig. 1. Although a green solution also formed in dipolar aprotic solvents such as DMF and pyridine, DMSO was the most effective solvent among them, because of the good solubility of KOH. The color of the solution immediately turned from green to orange, the original color, after the addition of water, and **1** was nearly quantitatively recovered (Table 3, Entry 1). Although Shah reported the formation of indanthrone from **1** and KOH in DMSO at 60 °C4,5), no

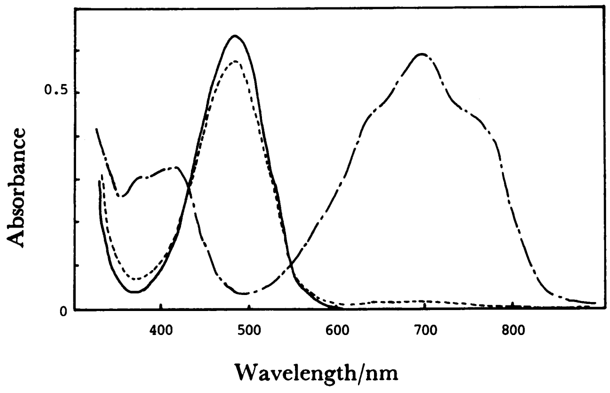
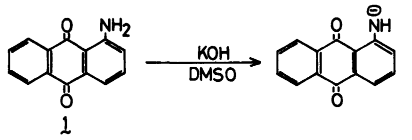


Fig. 1. Absorption spectra of **1** in DMSO.
[**1**]=*ca.* $1\times10^{-4}\ \mathrm{mol\cdot dm^{-3}}$. KOH free (——), in the presence of KOH(– – –), addition of H_2O into KOH–DMSO system(----).

indanthrone was observed in our system. In the green solution no paramagnetic species was detected by an ESR measurement. These results ruled out Brunner and Deffner's proposal[7] that the color change was caused by the formation of a charge-transfer complex between **1** and the carbanion of DMSO ($CH_3SO\overset{\ominus}{C}H_2$). Further, after the addition of alkyl halide to the green solution, it became red and an *N*-alkylated product was obtained in good yield at room temperature (*vide infra*). Consequently, we concluded that the color change of **1** in an KOH-DMSO solution was undoubtedly caused by the loss of a proton from the amino group to afford the amide ion:



(1)

Similar results were also obtained in the case of 2-aminoanthraquinone(**5**); that is, the new absorption band appeared in the region of 550—850 nm (Table 1) and disappeared after the addition of water. The resulting green solution also afforded an *N*-alkylated product after the addition of an alkyl halide. Although Bradley reported that **5** exhibited no alkali color reaction in a pyridine containing methanolic KOH,[8] our results indicated that the amino group of **5** was easily deprotonated in an KOH-DMSO solution to give the amide ion.

Monoalkylaminoanthraquinones(**2** and **6**) also gave green solution on being mixed with powdered KOH in DMSO. Although the color returned to the original one after the addition of water, a TLC examination showed both the recovered one and the dealkylated product(**1** or **5**). These results show that the dealkylation occurs under basic conditions, although (monoalkylamino)anthraquinones have been known to give the dealkylated products under acidic conditions.[9]

The color of 1-dimethylaminoanthraquinone(**3**), having no N-H bond, was little affected by the addition of powdered KOH in DMSO. This result also supports the idea that the color changes of aminoanthraquinones were caused by the loss of a proton from the amino group to afford the amide ion.

Table 1. Absorption spectra of aminoanthraquinones in the presence of powdered KOH in DMSO

AQs	λ_{max}/nm		
	in DMSO	in KOH-DMSO	
		under air	under N_2
AQ	326	—	552, 515(sh), 410(sh), 393
1-NH_2AQ (**1**)	482	695	568, 510
1-CH_3NHAQ (**2**)	509	695	560, 510
2-NH_2AQ (**5**)	456	670	545, 432, 408
2-C_4H_9NHAQ (**6**)	474	706	545, 471

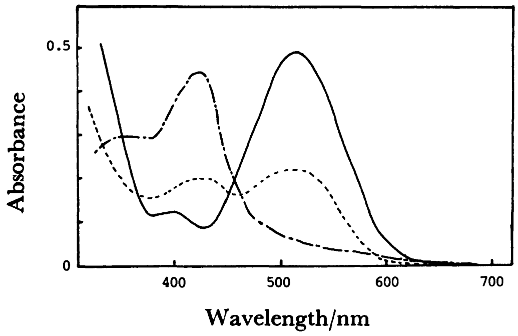
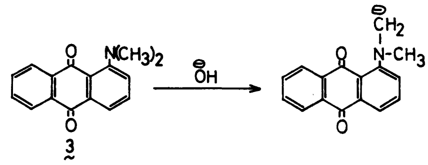


Fig. 2. Absorption spectra of **3** in DMSO.
[**3**]=*ca.* 1×10^{-4} mol·dm^{-3}. KOH free(——), in the presence of KOH pretreated with methanol(— — —), addition of H_2O into KOH-DMSO system(- - - -).

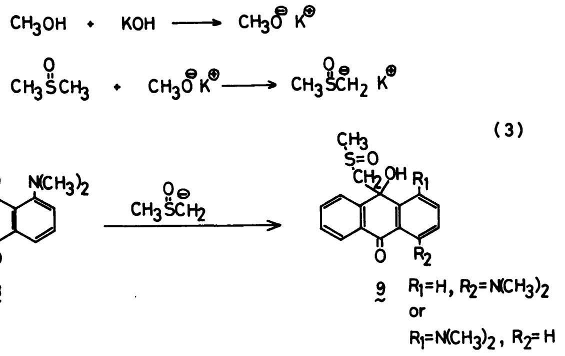
The Reaction of (Dialkylamino)anthraquinones with DMSO. In order to prepare a fine KOH powder, KOH was dissolved in anhydrous methanol and then methanol was evaporated *in vacuo*. When **3** was mixed with the resulting fine, white KOH powder in DMSO, the color immediately changed from red to yellow. Figure 2 shows that the absorption band (510 nm) of **3** disappeared and a new band appeared at 420 nm. The color change was hypsochromic, contrary to the formation of amide ion. Since no radicals were detected in the yellow solution during ESR measurements, the yellow species could not be the radical anion.

After the addition of D_2O to the yellow solution of **3**, the absorption spectra did not return to the original state and a TLC examination indicated two spots, red and yellow. It was found that the mass spectrum of the red component was identical with that of **3** and no deuteration took place. This result showed that the hypsochromic change was not attributed to the formation of the carbanion of aminomethyl group of **3**:



(2)

These color changes were not observed in a DMF solution. This result indicated that DMSO was responsible for the hypsochromic changes. The mass spectra[*m/z* 329(M+), 251, 78] clearly indicated that the yellow hygroscopic compound was an 1 : 1 adduct of **3** and DMSO. Actually, sulfur atoms were detected using the standard method with lead acetate. The IR spectrum showed the appearances of a hydroxyl group (3250 cm^{-1}) and a sulfinyl group (1015 cm^{-1}). ^{1}H NMR analysis also supported the idea that the new yellow compound was a DMSO addition compound(**9**). However, the definitive evidences whether the addition occurred at 9- or 10-carbonyl group of **3** could not be obtained. These results indicated that potassium methylsulfinylmethanide ($CH_3SO\overset{\ominus}{C}H_2K^{\oplus}$) was formed by the reaction of DMSO with KOH pretreated with methanol (probably potassium methoxide[10]) and reacted with **3** to yield DMSO addition compound(**9**) as shown in Eq. 3.



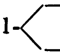
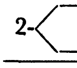
(3)

It has been reported that methylsulfinylmethanide, formed by the reaction of DMSO with potassium *t*-butoxide or sodium hydride, reacted quantitatively with benzophenone to yield the β-hydroxy sulfoxide.[11]

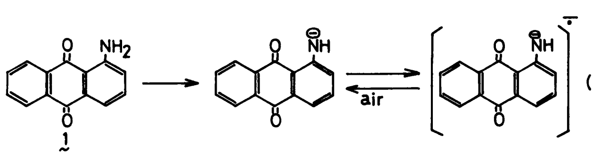
A similar hypsochromic change was also observed in the case of (dialkylamino)anthraquinones(**4**, **7**, and **8**)(Table 2). However, the color changes of aminoanthraquinones(**1**, **2**, **5**, and **6**), which were caused by the KOH pretreated with methanol, were the same as those treated with powdered KOH. These results indicate that methylsulfinylmethanide does not attack the amide ions.

The Formation of Radical Species under a Nitrogen Atmosphere. When anthraquinone was mixed with powdered KOH in DMSO under a nitrogen atmosphere, a red solution immediately resulted. The red solution showed a well-resolved ESR spectrum: The hyperfine coupling constants were $a_{H_1}=0.94$ G(1 G=10^{-4} T) and $a_{H_2}=0.29$ G. These values almost agreed with those of anthraquinone radical anion generated by electrochemical reduction.[12] These results suggest that aminoanthraquinones may be reduced to the radical anion in KOH-DMSO solution under a nitrogen atmosphere.

TABLE 2. ABSORPTION SPECTRA OF DIALKYLAMINOANTHRAQUINONES IN THE PRESENCE OF POWDERED KOH PRETREATED WITH METHANOL IN DMSO

AQs	λ_{max}/nm in DMSO	in KOH-DMSO under air	in KOH-DMSO under N_2
1-$(CH_3)_2$NAQ (**3**)	510	420	568, 535(sh), 402
1-NAQ (**4**)	520	405	569, 535(sh), 401, 387
2-$(C_4H_9)_2$NAQ (**7**)	491	372	542, 506(sh), 338
2-NAQ (**8**)	477	386	549, 510(sh), 397

Under a N_2 atmosphere the color of **1** rapidly changed from orange to green similar to a system under air when mixed with powdered KOH in DMSO. This green solution, however, slowly turned to violet. The spectral changes are shown in Fig. 3. The violet solution was paramagnetic(g=2.003) and showed well-resolved ESR spectrum (Fig. 4). When air was bubbled through the violet solution, it became green and no radical species were detected. Further the addition of water caused this aerated solution to change from green to orange. These results revealed that the radical species was not a radical anion of **1**, but one of the amide ions:



(4)

A radical anion would be formed by an electron transfer from a naked hydroxide ion to the amide ion.

The (monoalkylamino)anthraquinones(**2** and **6**)

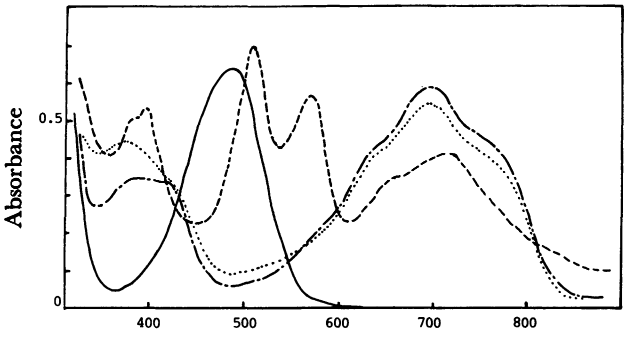


Fig. 3. Absorption spectra of **1** in DMSO under nitrogen atmosphere.

[**1**]=*ca.* 1×10^{-4} mol·dm^{-3}. KOH free(——), in the presence of KOH after 9 min(— — —), after 20 h(- - - -), air was bubbled into the solution after 20 h(······).

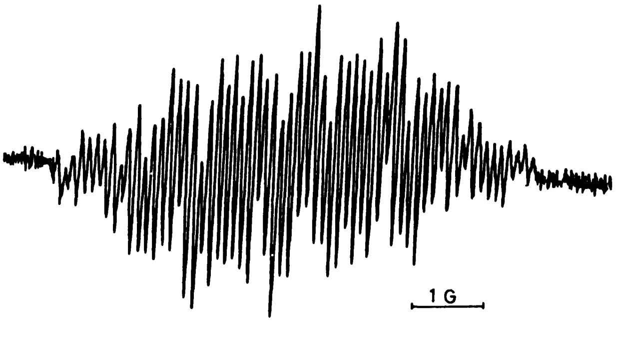


Fig. 4. ESR spectrum of the radical species of **1** in KOH–DMSO system under nitrogen atmosphere.

changed to the radical anions of their amide ions more rapidly than **1** and **5**. The spectral data are shown in Table 1. The colors of (dialkylamino)anthraquinones(**3**, **4**, **7**, and **8**) did not change in powdered KOH-DMSO system, while those in the presence of KOH pretreated with methanol in DMSO rapidly changed from red to yellow and then to violet. By the introduction of air into violet solution, a yellow solution was reproduced. The radical species would be the radical anion of the yellow DMSO addition compound.

The N*-Alkylation of Aminoanthraquinones* via *their Amide Ions.* The amide ions formed in an KOH-DMSO system would be easily N-alkylated by alkyl halides. The compound(**1** or **5**) was first converted to its amide ion by treating it with powdered KOH in DMSO under air. Then, excess alkyl halide was added at 30 °C. Table 3 lists the results of N-alkylation. In KOH-free systems the yields were negligibly small. However, the yields dramatically increased after the addition of powdered KOH. This result confirmed that the amino group of **1** and **5** was deprotonated in the KOH-DMSO system.

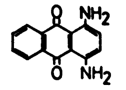
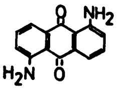
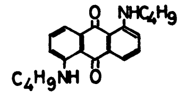
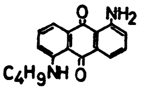
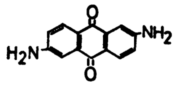
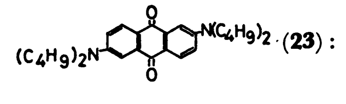
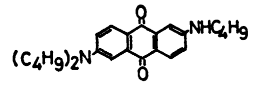
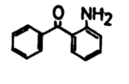
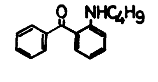
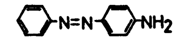
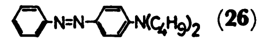
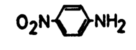
Table 3 shows that **1** was converted to its monoalkylamino derivatives while **5** gave the (dialkylamino)anthraquinones in high yields. The different reactivities between **1** and **5** toward alkyl halides may be explained as follows. 1-Alkylaminoanthraquinone was also deprotonated to give its amide ion, but the attack of alkyl halide to the amide ion may be

TABLE 3. N-ALKYLATION OF AMINOANTHRAQUINONES IN KOH-DMSO SYSTEM[a)]

Entry	AQ	RX	t/min	Recovered NH_2AQ/%	Product	Yield/%
1	1-NH_2AQ (**1**)	—	90	92	—	—
2[b)]	1-NH_2AQ (**1**)	n-C_4H_9I	60	96	1-C_4H_9NHAQ (**16**)	3
3	1-NH_2AQ (**1**)	n-C_4H_9I	5	0	1-C_4H_9NHAQ (**16**)	75
4	1-NH_2AQ (**1**)	n-C_4H_9I	60	0	1-C_4H_9NHAQ (**16**)	52
5	1-NH_2AQ (**1**)	n-$C_{16}H_{33}Br$	60	0	1-$C_{16}H_{33}NHAQ$ (**17**)	51
6	1-NH_2AQ (**1**)	n-$C_{16}H_{33}Br$	450	0	1-$C_{16}H_{33}NHAQ$ (**17**)	34
7	2-NH_2AQ (**5**)	—	90	95	—	—
8[b)]	2-NH_2AQ (**5**)	n-C_4H_9I	60	90	2-C_4H_9NHAQ (**18**)	7
9	2-NH_2AQ (**5**)	n-C_4H_9I	5	0	2-C_4H_9NHAQ (**18**)+ 2-$(C_4H_9)_2NAQ$ (**19**)	8 87
10	2-NH_2AQ (**5**)	n-C_4H_9I	60	0	2-$(C_4H_9)_2NAQ$ (**19**)	93
11	2-NH_2AQ (**5**)	n-$C_{16}H_{33}Br$	60	0	2-$(C_{16}H_{33})_2NAQ$ (**20**)	70
12	2-NH_2AQ (**5**)	n-$C_{16}H_{33}Br$	450	0	2-$(C_{16}H_{33})_2NAQ$ (**20**)	88

a) AQ = 1 mmol, RX = 10 mmol, KOH = 10 mmol, DMSO = 30 ml, temp 30 °C. b) KOH-free system.

TABLE 4. N-ALKYLATION WITH n-BUTYL IODIDE IN KOH-DMSO SYSTEM[a)]

Substrate	t/min	Product: Yield/%
 (**10**)	30	—[b)]
 (**11**)	30	 (**21**): 77 +  (**22**): 8
 (**12**)	30	 (**23**): 69 +  (**24**): 14
 (**13**)	60	 (**25**): 84
 (**14**)	60	 (**26**): 79
 (**15**)	60	 (**27**): 81

a) Substrate = 1 mmol, n-C_4H_9I = 10 mmol, KOH = 10 mmol, DMSO = 30 ml, at 30 °C. b) Several unidentified products were obtained.

sterically hindered by the adjacent carbonyl group. On the other hand, the alkylation of the amide ion of **5** is insensitive to such a steric factor. Consequently, **5** was easily converted into its dialkylamino derivatives, while the *N*-alkylation of **1** stopped at the stage of monoalkylation. When the reaction of **5** with butyl iodide was quenched with water after 5 min, 2-butylaminoanthraquinone was also obtained together with 2-dibutylaminoanthraquinone (Table 3, Entry 9). Table 3 also shows that the yield of *N*-alkylation of **1** decreased with the increase of the reaction time, contrary to the reaction of **5**.

The *N*-alkylation of diaminoanthraquinones also took place under similar conditions. 1,4-Diaminoanthraquinone(**10**) changed from violet to marine blue, 1,5-diaminoanthraquinone(**11**) from red to cobalt blue, and 2,6-diaminoanthraquinone(**12**) from orange to dark green in KOH–DMSO solution. By the addition of butyl iodide, **11** and **12** were easily *N*-alkylated, but in the reaction of **10** several unidentified products were formed. Table 4 shows that 1-amino group suffered monoalkylation and 2-amino group suffered dialkylation in analogy with monoaminoanthraquinone(**1** and **5**).

N-*Alkylation of Aromatic Amines with Electron-withdrawing Group.* The *N*-alkylation of aromatic amines activated by the electron-withdrawing group would also be expected by using an KOH–DMSO system. The color of 2-aminobenzophenone(**13**) was changed from yellow to red, *p*-aminoazobenzene(**14**) from orange to deep red, and *p*-nitroaniline(**15**) from yellow to orange when treated with powdered KOH in DMSO. The results of *N*-alkylation of these amines are shown in Table 4. Table 4 shows the very similar results to the case of aminoanthraquinones, that is, **13** underwent mono-*N*-alkylation, while **14** and **15** underwent di-*N*-alkylation.

TABLE 5. PHYSICAL PROPERTIES AND ANALYTICAL DATA OF ALKYLAMINOANTHRAQUINONES AND ALKYLAMINOAROMATICS

Compound	^{1}H NMR (δ) in $CDCl_3$	Formula	MS m/z(M$^+$)		Calcd (%)	Found (%)
16a)	0.8—1.9(7H, m, $CH_2C_3\underline{H}_7$), 3.0—3.4(2H, m, $NC\underline{H}_2$),	$C_{18}H_{17}NO_2$	279	C:	77.39	77.56
	6.7—8.3(7H, m, aromatic), 9.64(1H, br s, N$\underline{H}$)			H:	6.14	6.20
				N:	5.02	4.91
17a)	0.6—1.9(31H, m, $CH_2C_{15}\underline{H}_{31}$), 3.0—3.4(2H, m, $NC\underline{H}_2$)	$C_{30}H_{41}NO_2$	447	C:	80.49	80.21
	6.7—8.8(7H, m, aromatic), 9.6(1H, br s, N$\underline{H}$)			H:	9.23	9.52
				N:	3.13	3.10
18b)	——	$C_{18}H_{17}NO_2$	279	C:	77.39	77.00
				H:	6.14	6.01
				N:	5.02	4.83
19a)	0.7—2.0(14H, m, $CH_2C_3\underline{H}_7$), 3.33(4H, t, $NC\underline{H}_2$)	$C_{22}H_{25}NO_2$	335	C:	78.77	78.90
	6.6—8.3(7H, m, aromatic)			H:	7.51	7.39
				N:	4.18	4.07
20a)	0.7—2.1(62H, m, $CH_2C_{15}\underline{H}_{31}$), 3.40(4H, t, $NC\underline{H}_2$)	$C_{46}H_{73}NO_2$	672	C:	82.21	81.98
	6.6—8.3(7H, m, aromatic)			H:	10.95	11.38
				N:	2.08	2.03
21	0.8—2.0(14H, m, $CH_2C_3\underline{H}_7$), 3.1—3.5(4H, m, $NC\underline{H}_2$)	$C_{22}H_{26}N_2O_2$	350	C:	75.40	75.42
	7.0—7.8(7$\underline{H}$, m, atomic), 9.88(1H, br s, NH)			H:	7.48	7.40
				N:	7.99	7.87
22	0.8—2.1(7H, m, $CH_2C_3\underline{H}_7$), 3.1—3.6(2H, m, $NC\underline{H}_2$)	$C_{18}H_{18}N_2O_2$	294	C:	73.45	73.61
	6.6—7.9(8H, m, aromatic), 9.9(1H, br s, NH)			H:	6.16	6.32
				N:	9.52	9.27
23	0.8—1.9(21H, m, $CH_2C_3\underline{H}_7$), 3.50(8H, t, $NC\underline{H}_2$)	$C_{30}H_{42}N_2O_2$	462	C:	77.88	77.60
	6.8—8.3(6H, m, aromatic)			H:	9.15	8.99
				N:	6.05	5.85
24	0.8—1.9(21H, m, $CH_2C_3\underline{H}_7$), 3.1—3.7(6H, m, $NC\underline{H}_2$)	$C_{26}H_{34}N_2O_2$	406	C:	76.81	76.65
	4.60(1H, br s, NH), 6.8—8.3(6H, m, aromatic)			H:	8.43	8.24
				N:	6.88	6.71
25	0.7—2.1(7H, m, $CH_2C_3\underline{H}_7$), 3.25(2H, t, $NC\underline{H}_2$)	$C_{17}H_{19}NO$	253		——	
	6.4—8.1(9H, m, aromatic), 8.69(1H, br s, NH)					
26	0.7—2.0(14H, m, $CH_2C_3\underline{H}_7$), 3.34(2H, t, $NC\underline{H}_2$)	$C_{20}H_{27}N_3$	309		——	
	6.6—8.1(9H, m, aromatic)					
27	0.7—1.9(14H, m, $CH_2C_3\underline{H}_7$), 3.34(4H, t, $NC\underline{H}_2$)	$C_{14}H_{22}N_2O_2$	250		——	
	6.53(2H, d, aromatic), 8.01(2H, d, aromatic)					

a) NMR data in CCl_4. b) The NMR spectra could not be measured because of low solubility.

Although the *N*-alkylation of nitrogen heterocyclic compounds and aromatic amines by the use of various bases has been reported,[13] these results indicate that the reaction using an KOH–DMSO system affords a rapid, simple, and mild method of *N*-alkylation of aromatic amines.

Experimental

Materials. Commercial reagent-grade chemicals were used without further purification. Dimethyl sulfoxide was distilled twice under reduced pressure and stored under a nitrogen atmosphere. Aminoanthraquinones (Sumitomo Chemical Co.) were purified as follows: **1** and **2** were purified by alumina column chromatography and recrystallized from benzene. The compounds **10** and **11** were purified by recrystallization from toluene. The purification of **5** and **12** were performed by Maki's method.[14] Compound **3** was prepared by the condensation of 1-chloroanthraquinone and dimethylamine in ethanol and purified by column chromatography on silica gel with benzene as eluent and recrystallized from ethanol (Found: C, 76.53; H, 5.16; N, 5.50%). The Preparation of **4** and **8** were performed by the reaction of 1- and 2-chloroanthraquinone with piperidine and purified by column chromatography on silica gel and recrystallized from ethanol (Found: **4**; C, 78.24; H, 5.88; N, 4.86%. **8**; C, 78.13; H, 5.71; N, 4.63%). The compound **13** was prepared according to the literature[15].

Instruments. Visible spectra were recorded with a Shimadzu UV-210 spectrometer. ^{1}H NMR spectra were measured with a Hitachi R-24 spectrometer in $CDCl_3$ and CCl_4 with tetramethylsilane and in D_2O with sodium 3-trimethylsilyl-1-propanesulfonate as an internal standard. IR spectra were recorded on a JASCO IRA-1 spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 100 mass spectrometer by direct insertion. The ESR spectra were taken on a JEOL-PE-3X instrument, equipped with a 100 KHz field modulation unit. Elementary analyses were performed on a Yanaco MT2 CHN corder.

Reaction of 1-Dimethylaminoanthraquinone. Powdered KOH 560 mg (10 mmol) was dissolved in anhydrous methanol (20 ml) and then solvent was evaporated under reduced pressure. The fine, powdered KOH was dissolved in 100 ml of DMSO. 251 mg (1 mmol) of **3** was added to the solution and stirred for 10 min at room temperature. The resulting orange mixture was poured into water (700 ml), followed by extraction with benzene several times. After the benzene was evaporated, the residue was chromatographed on a silica gel by employing first benzene and then benzene–ethanol(20+1) as eluents. The early red fractions contained 28 mg of the starting material **3** (11%). The later yellow fractions contained 279 mg of DMSO addition compound(**9**)(85%). The spectral properties of **9** are as follows: ^{1}H NMR(D_2O) 2.34 (s, 3H), 2.84 (s, 6H), 3.36 (s, 2H), 6.9—8.1 (m, 7H). IR(KBr) 3250, 1640, 1268, 1015, 785, 695 cm^{-1}. MS(m/z) 329(M+), 312, 251, 248, 78. UV(C_2H_5OH) 424 nm.

Procedure for N-*Alkylation.* A typical procedure is described for the reaction of **1** with butyl iodide. The compound **1** (1 mmol) was stirred with powdered KOH (10 mmol) in DMSO (30 ml) for 30 min at 30 °C. The color of the mixture changed rapidly from red to green. Then, butyl iodide (10 mmol) was added to the mixture and the solution was stirred for 5 min at 30 °C. By the addition of butyl iodide, the color of the solution turned to dark red and the reaction was quenched with water (700 ml). The mixture was then extracted with benzene several times, washed with water and evaporated. Then the residue was submitted to column chromatography on silica gel using benzene as the eluent. The physical properties and analytical data for the *N*-alkylated products are given in Table 5.

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References

1) A part of this work has been reported in a preliminary form: S. Arai, T. Yamagishi, and M. Hida, *Chem. Lett.*, **1981**, 1789.

2) S. Kato, H. Inoue, and M. Hida, *Nippon Kagaku Kaishi*, **1978**, 1411.

3) W. Bradley and H. E. Nursten, *J. Chem. Soc.*, **1951**, 2170.

4) M. K. Shah and K. H. Shah, *Indian J. Technol.*, **13**, 312 (1975).

5) D. C. Mansharamani, M. K. Shah, and K. H. Shah, *J. Indian Chem. Soc.*, **53**, 1671 (1976).

6) Powdered KOH was prepared by grounding a commercial KOH (Tokyokasei GR) with an ordinary mortar and pestle, followed by vacuum drying.

7) E. Brunner and U. Deffner, *Melliand Textilber. Int.*, **50**, 437 (1969).

8) W. Bradley, *J. Soc. Dyers Colour.*, **58**, 2 (1951); W. Bradley and E. Leete, *J. Chem. Soc.*, **1951**, 2129.

9) W. Bradley and R. F. Maisey, *J. Chem. Soc.*, **1954**, 247.

10) J. C. R. Kelly and P. E. Snyder, *J. Am. Chem. Soc.*, **73**, 4114 (1951).

11) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962); A. Ledwith and N. McFarlane, *Proc. R. Soc. London, Ser. A.*, **1964**, 108.

12) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

13) K. Sukata, *Bull. Chem. Soc. Jpn.*, **56**, 280 (1983), and references therein.

14) T. Maki, *Kogyo Kagaku Zasshi*, **36**, 174 (1933).

15) *Org. Synth.*, Col. Vol. **IV**, 34.