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Syntheses of Nitrogen-containing Heterocyclic Compounds. XLI.[1] Reaction of Diazaphenanthrenes and Their N-Oxides with Methylsulfinyl Carbanion[2]

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The reactions of 4,6-phenanthroline (I) and its N-oxides, 6-oxide (II) and 4,6-dioxide (IV), with dimethyl sulfoxide were carried out in the presence of sodium hydride (or potassium *tert*-butoxide), and 3-monomethyl compounds (V, VI, and IX) were obtained from all the compounds. This reaction of the 4-oxide (III) resulted in deoxygenation of the N-oxide group to afford the 3,5-dimethyl compound (VII) and 5-(methylsulfinyl)-methyl-4,6-phenanthroline (VIII). The same reaction of 1,10-, 1,7-, and 4,7-phenanthrolines (X, XI, XII) gave the 4-methyl compound (XVI) and 4,7-dimethyl compound (XVII) from X, and the 4-methyl compound (XVII) and 7-(methylsulfinyl)methyl compound (XIX) from XI, while XII gave a polymer. The reaction of their N-oxides, 1,10-phenanthroline 1-oxide (XIII), 1,7-phenanthroline 1-oxide (XIV), and 4,7-phenanthroline 7-oxide (XV), for 30 min resulted in liberation of the N-oxide group to form benzo[*h*]quinoline (XX) in the former two cases and benzo[*f*]quinoline (XXIII) in the latter case.

Reaction of XIII for 4 hr resulted in the formation of compounds of XX methylated at the 6- or 5-position (XXI and XXII). The same reaction was carried out in an NMR sample tube, and it was shown that N-oxide liberation occurred in the reaction mixture; the previously proposed reaction mechanism had to be corrected. Calculation of the reaction indices of 4,6-phenanthrolines by Hückel's molecular orbital method gave values agreeing well with the experimental results.

Keywords——methylsulfinyl carbanion; liberation of the N-oxide group; 4,6-phenanthroline; *o*-phenanthroline; *m*-phenanthroline; *p*-phenanthroline; 1,10-phenanthroline; 1,7-phenanthroline; 4,7-phenanthroline; Hückel's molecular orbital calculations

We have previously studied the reaction of monoazaphenanthrenes and their N-oxides with methylsulfinyl carbanion and reported a new reaction resulting in liberation of the N-oxide group in the latter compounds, differing from the reaction of the former compounds.[4] In the present work, we reacted diazaphenanthrenes and their N-oxides with methylsulfinyl carbanion. Calculation of the reactivity index by Hückel's molecular orbital (HMO) method gave values agreeing with the experimental results.

4,6-Phenanthroline (benzo[*f*][1,7]naphthyridine) (I) was taken as a diazaphenanthrene and, in order to compare their reactivities, its N-oxides,[5] 6-oxide (II), 4-oxide (III), and 4,6-dioxide (IV), were allowed to react with methylsulfinyl carbanion.

Reaction of I and II with methylsulfinyl carbanion was carried out using sodium hydrdie at 70° for 4 hr (method A), as shown in Chart 1. Compound V was obtained from I in 46.4% yield but only a structurally unknown polymer was obtained from II. Therefore, II was allowed to react with potassium *tert*-butoxide at room temperature for 4 hr (method B),

1) Part XL: M. Sugiura, Y. Hamada, and M. Hirota, *Chem. Pharm. Bull.* (Tokyo), **27**, 1518 (1979).
2) *a*) A part of this work was presented at the 8th Congress on Heterocyclic Chemistry, Kyoto, Oct. 1975; *b*) Presented at the 28th Congress on Organic Chemical Reaction Mechanisms, Yokohama, Nov. 1977.
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4) Y. Hamada and I. Takeuchi, *J. Org. Chem.*, **42**, 4209 (1977).
5) Y. Hamada and I. Takeuchi, *Chem. Pharm. Bull.* (Tokyo), **24**, 2769 (1976).

yielding VI in 53.1% yield. Both V and VI were found to be monomethyl compounds on the basis of elemental analyses and mass spectral measurements. Nuclear magnetic resonance (NMR) spectra of V and VI were compared with those of I and II, respectively, and from the disappearance of the 5-H proton signal at the lowest magnetic field, it was clear that the 5-position of both compounds had been methylated. The N-oxide compound obtained by oxidation of V with hydrogen peroxide and sodium tungstate showed no depression of melting point when fused with VI, and their infrared (IR) spectra were identical.

Reaction of III with methylsulfinyl carbanion by method A gave VII in 2.5% yield, while VIII was obtained in 38.3% yield by method B. Compound VII was found to be a deoxygenated dimethyl compound from its elemental analysis and mass spectrum; comparison of its NMR spectrum with that of I indicated the disappearance of the 5-H proton signal and the appearance of 1- and 2-H protons as a doublet at 8.94 and 7.80 ppm (J_{1-2}=8.8 Hz). Signals of the methyl groups were observed at 2.93 and 3.27 ppm. From these data, VII

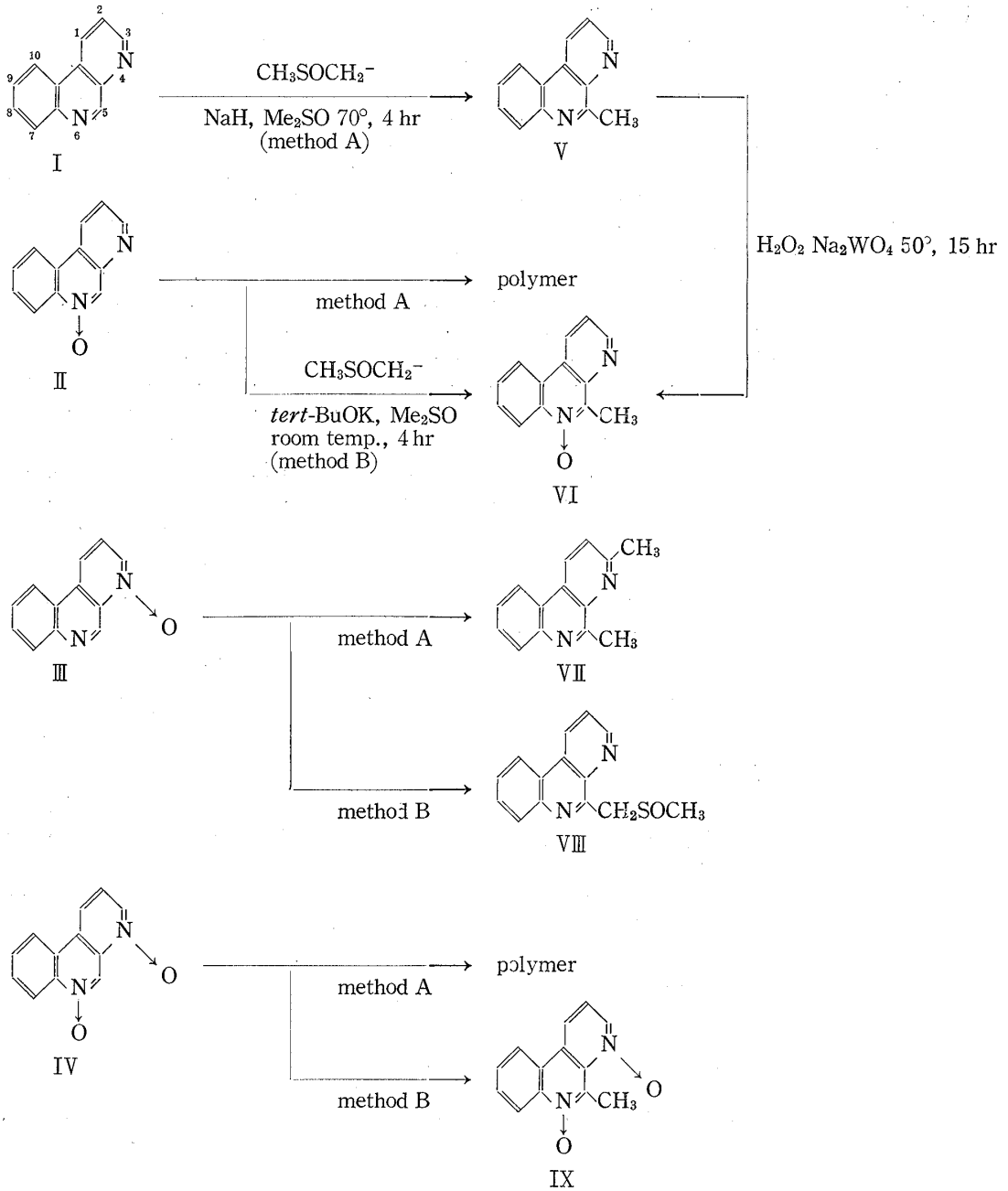

Chart 1

was assigned as 3,5-dimethyl-4,6-phenathroline. Compound VIII was found to correspond to the molecular formula $C_{14}H_{12}N_2OS$ from its analytical values and mass spectrum, with *m/e* 256 (M^+), 193 (M^+–$SOCH_3$), and 179 (M^+–CH_2SOCH_3), and its IR spectrum (in chloroform) showed absorption due to S=O at 1030 cm^{-1}. Comparison of the NMR spectrum of VIII with that of I showed disappearance of the 5-H proton signal, with a methyl signal at 2.77 ppm, and the signals of geminal methylene protons as a doublet at 4.84 and 5.18 ppm. These data suggested VIII to be 5-(methylsulfinyl)methyl-4,6-phenanthroline.

The reaction of IV with methylsulfinyl carbanion by method A gave only a polymer of unknown structure, but IX was obtained in 22.2% yield by method B. Elemental analysis and the mass spectrum indicated IX to be a monomethyl compound and IX was confirmed to be a 5-methyl compound from its NMR spectrum.

Details of these experiments are illustrated in Chart 1 and the data are given in Table I.

TABLE I. NMR Spectral Data for 4,6-Phenanthrolines

Compd. No.	Solvent	Chemical shift (ppm)										Coupling constants (Hz)			
		H-1	H-2	H-3	H-5	H-7	H-8	H-9	H-10	3-CH_3	5-CH_3	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	J_{CH_2SO}
I	$CDCl_3$	8.82	7.70	9.00	9.48	8.22	7.74	7.74	8.44	—	—	8.4	2.0	4.4	
V	$CDCl_3$	8.77	7.66	9.02	—	8.16	7.72	7.72	8.38	—	3.15	8.4	2.0	4.4	
VI	$CDCl_3$	8.55	7.47	8.86	—	8.78[a]	7.68	7.68	8.28	—	3·07	8.0	1.8	4.4	
VII	$CDCl_3$	8.94	7.80	—	—	8·33	7.33	7.33	8.64	2.92	3.25	8.8	—	—	
										CH_2SOCH_3					
VIII	$CDCl_3$	8.72	7.63	8.89	—	8.07	7.66	7.66	8.33	$\binom{4.84}{5.18}$[b]	2.77	8.2	1.6	4.0	12.0
IX	$(CD_3)_2SO$	8.68	7.68	8.62	—	8.82[a]	7.94	7.94	8.68	—	3.30	8.0	1.8	6.0	

a) Anisotropic effect of the N–O group.
b) Geminal methylene protons.

Reaction with methylsulfinyl carbanion was then carried out with 1,10-, 1,7-, and 4,7-phenanthrolines (*o*-, *m*-, and *p*-phenanthrolines) (X, XI, and XII), and their mono-N-oxides, 1,10-phenanthroline 1-oxide (XIII), 1,7-phenanthroline 1-oxide (XIV), and 4,7-phenanthroline 7-oxide (XV). Under the conditions of method A, a dimethyl compound (XVII) was obtained in a better yield of 41% than that (10%) of the monomethyl compound (XVI) from X. Shortening the reaction time to 30 min resulted in the formation of XVI as a major product in 45% yield. The position of the methyl group in these compounds was deduced from their NMR spectral data (Table II). It was confirmed that XVI is a 4-methyl compound by comparison of its NMR spectrum with that of X; the disappearance of the 4-H proton signal in XVI and appearance of the 2- and 3-H protons as a doublet were noted. XVII was confirmed to be a 4,7-dimethyl compound similarly.

The reaction of XI with methylsulfinyl carbanion gave the expected 4-methyl compound (XVIII), together with another compound (XIX). Elemental analysis and the mass spectrum [*m/e* 256 (M^+), 193 (M^+–$SOCH_3$)] indicated XIX to have the molecular formula $C_{14}H_{12}N_2OS$, and its IR spectrum showed an absorption due to S=O at 1010 cm^{-1}. Comparison of the NMR spectrum of XIX with that of XI showed disappearance of the 10-H proton signal at the lowest field and the appearance of a methyl signal at 2.74 ppm as well as signals of geminal methylene protons as a doublet at 4.88 and 5.62 ppm. These data proved XIX to be 10-(methylsulfinyl)methyl-1,7-phenanthroline.

The same reaction of XII failed to afford any methyl derivatives and only a structurally unknown polymer was obtained.

The reaction of XIII with methylsulfinyl carbanion (4 hr) resulted in liberation of the N-oxide group, and benzo[*h*]quinoline (XX) was obtained in 4% yield, together with XXI

and XXII which are considered to be further methylated compounds of XX. Shortening the reaction time to 30 min in order to raise the yield of XX resulted in the formation of XX as a sole product in 48% yield.

The reactions of XIV and XV with methylsulfinyl carbanion also resulted in liberation of the N-oxide group to afford XX and XXIII in low yields of 6% and 2%, respectively. These compounds showed characteristics somewhat different from those of XIII. The structures of XX and the two methyl compounds, XXI and XXII, were identified by mixed melting point determinations and IR spectral comparison with authentic samples synthesized in our previous work.[4] The isolation yields of XXI and XXII do not represent reaction yields because their separation is difficult and pure samples were only obtained after repeated chromatography. Therefore, the NMR spectrum of a mixture of XXI and XXII was measured and the yield was calculated from the integral ratio (3: 1) of their methyl groups.

Details of these experiments are illustrated in Chart 2 and the data given in Table II.

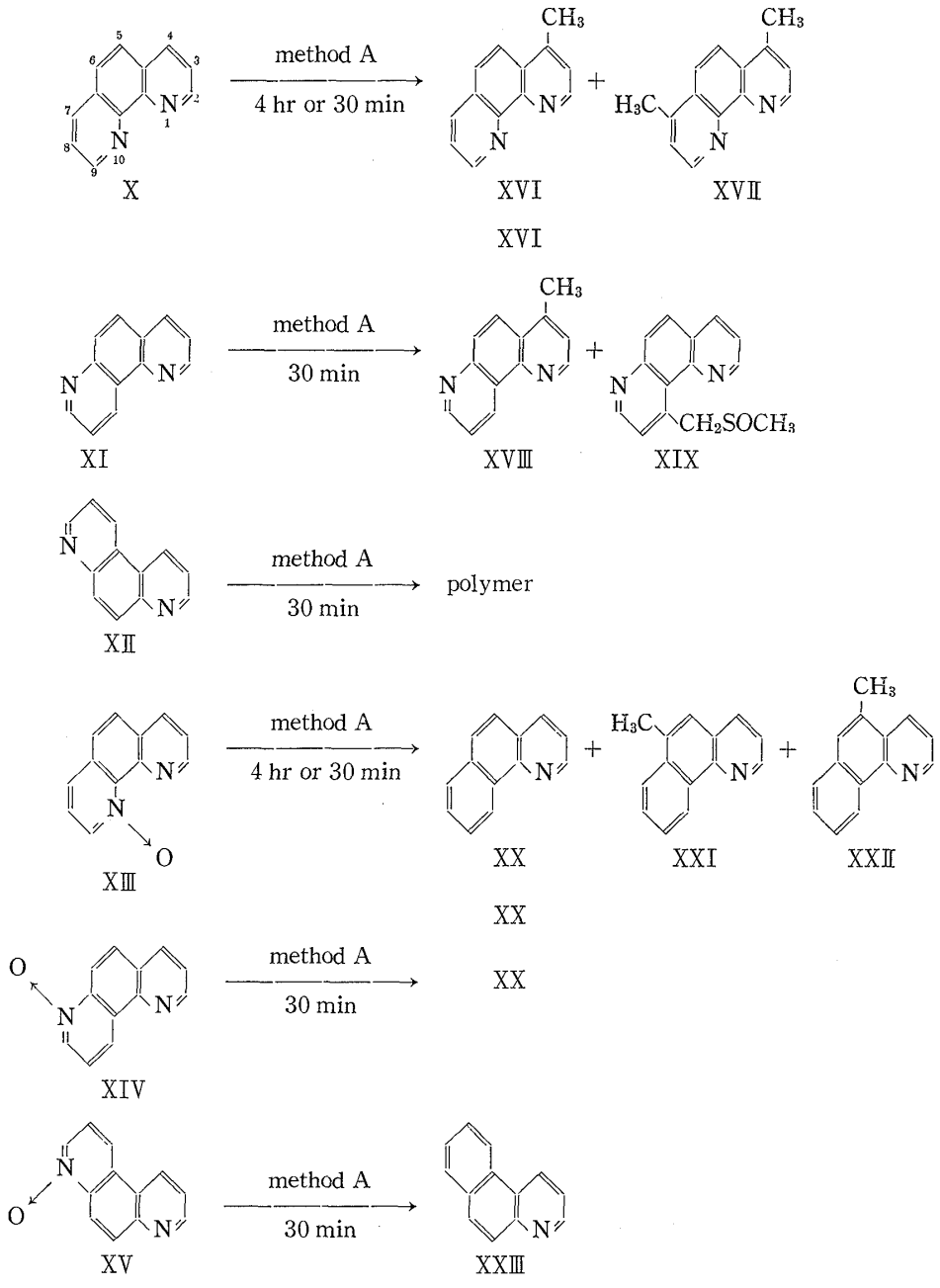

Chart 2

TABLE II. NMR Spectral Data for *o*- and *m*-Phenanthrolines in $CDCl_3$

Compd. No.	Chemical shift (ppm)										
	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10	4-CH_3	7-CH_3
X	9.10	7.52	8.11	7.63	7.63	8.11	7.52	9.10	—	—	—
XVI	8.97	7.37	—	7.67	7.89	8.13	7.53	9.11	—	2.70	—
XVII	8.82	7.24	—	7.76	7.76	—	7.24	8.82	—	2.63	2.63
XI	8.87	7.43	8.05	7.77	7.97	—	8.87	7.55	9.40	—	—
XVIII	8.66	7.22	—	7.92	7.92	—	8.85	7.47	9.35	2.65	—
XIX	8.91	7.53	8.20	7.87	8.07	—	8.92	7.53	—	CH_2SOCH_3 (4.88, 5.62)[a]	2.74

Compd. No.	Coupling constants (Hz)							
	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{5,6}$	$J_{7,8}$	$J_{7,9}$	$J_{8,9}$	J_{CH_2SO}
X	4.4	2.0	8.0	—	8.0	2.0	4.4	
XVI	4.4	—	—	8.8	8.0	1.8	4.0	
XVII	4.8	—	—	—	—	—	4.8	
					$J_{9,10}$	$J_{8,10}$	$J_{8,9}$	
XI	4.4	1.8	8.0	8.8	8.0	1.8	4.0	
XVIII	4.4	—	—	—	8.0	1.8	4.0	
XIX	4.4	1.8	7.6	8.8	—	—	4.6	11.0

a) Geminal methylene protons.

These experimental results indicate that the 5-position was active in the reaction of 4,6-phenanthrolines and methylsulfinyl carbanion, but the reaction of III by method A resulted in deoxygenation of the N-oxide group to form a dimethyl compound (VII). The reaction of III by method B also resulted in deoxygenation of the N-oxide group to form a (methylsulfinyl) methyl compound (VIII) but this was considered to be the result of a steric

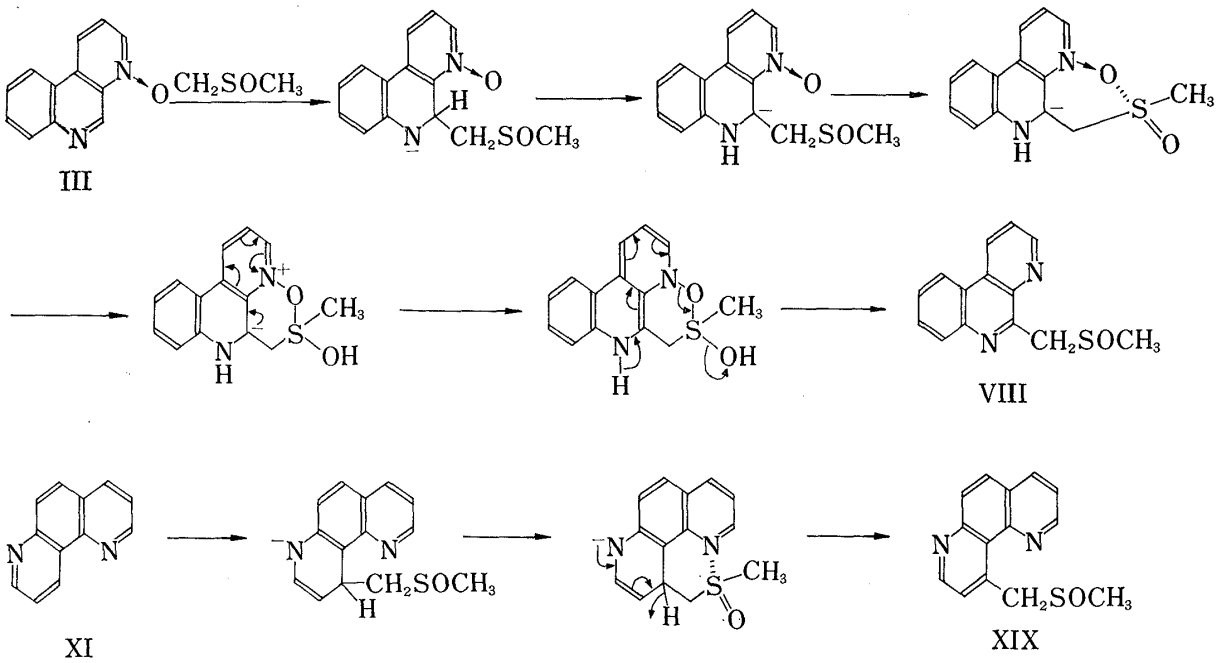

Chart 3

reaction, rather than a thermal deoxygenation. The mechanism illustrated in Chart 3 may be considered, in view of the reported mechanism for the reaction of quinoline and methylsulfinyl carbanion.[6] The reaction of XI and methylsulfinyl carbanion also afforded a (methylsulfinyl) methyl compound (XIX). In this case also, formation of a six-membered ring intermediate is easy and the (methylsulfinyl) methyl group was considered to have been stabilized to form XIX.

The anticipated liberation of the N-oxide group did not take place in the reaction of N-oxides of 4,6-phenanthrolines, but the expected compounds were obtained from mono-N-oxides of 1,10-, 1,7-, and 4,7-phenanthrolines. It is very interesting that the liberation of the N-oxide group depends on the position of the nitrogen atom in diazaphenanthrenes.

Examination of the Mechanism of Liberation of N-Oxides

In the reaction of benzo[*h*]quinoline N-oxide and methylsulfinyl carbanion, a reaction mechanism for the liberation of the N-oxide group has been proposed.[7] However, the results of the present series of experiments are inconsistent with the previous reaction mechanism, which involved a proton shift, so that the use of deuteracted dimethyl sulfoxide should result in the formation of D_1 and D_2 compounds in equal quantitties. Actually, however, only the D_1 compound, 4-deuteriophenanthrene, was obtained.[4] Even then, there

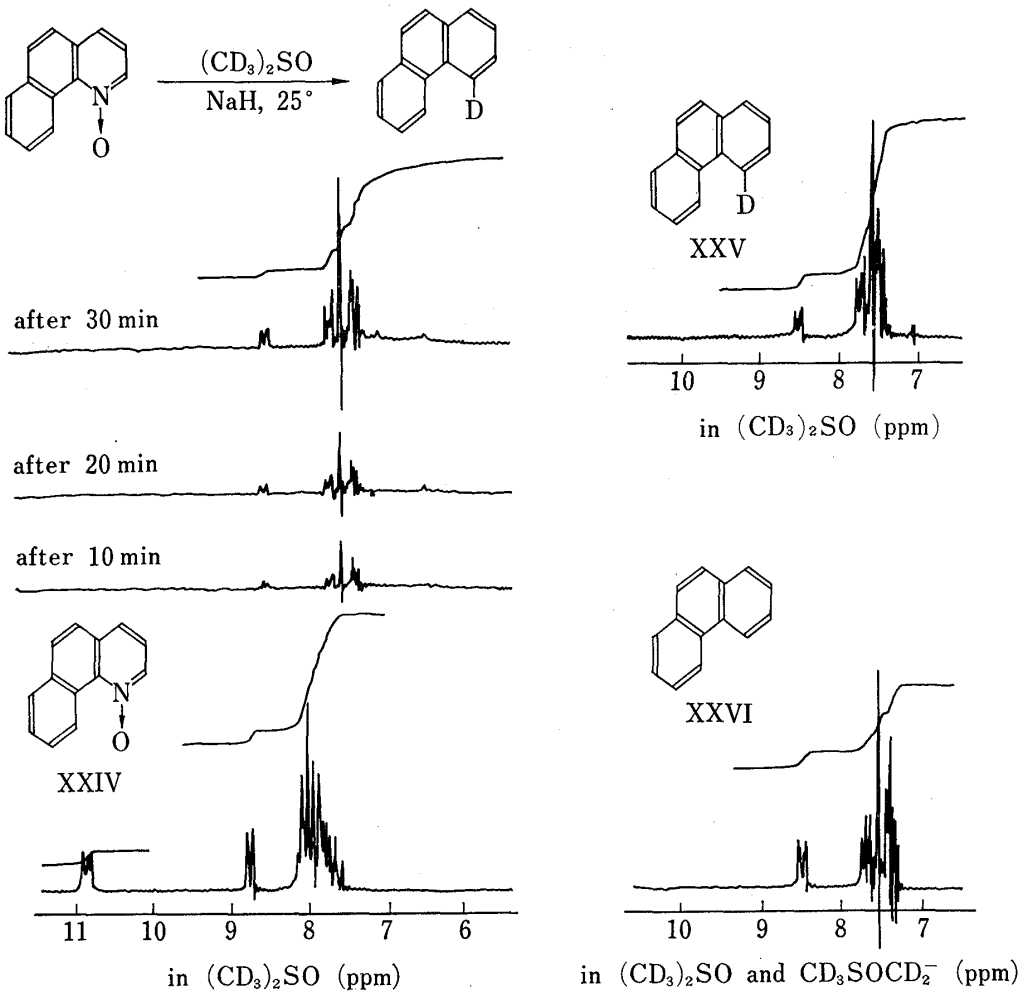

Fig. 1. NMR Spectra (100 MHz) of Reaction Mixture in an NMR Sample Tube

6) G.A. Russell and S.A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).
7) Y. Hamada, I. Takeuchi, and M. Hirota, *Tetrahedron Lett.*, **1974**, 495.

was a possibility that the D_2 compound might have been converted to the D_1 compound by the action of water, because water was added to decompose methylsulfinyl carbanion before working up the reaction mixture. In the present work, the reaction of XIII with methylsulfinyl carbanion suggested that liberation of the N-oxide group occurred before the addition of water to form XX, and XX was further methylated to form XXI and XXII. In fact, reaction of the parent compound X without an N-oxide group resulted in methylation at the 4- and 5-positions, *para* to the ring nitrogen, while in compound XIII with an N-oxide group, XIII methylated in the 5- and 6-positions was obtained in *ca.* 3:1 ratio,[4] although such methylation seems impossible before liberation of the N-oxide group. Therefore, in order to prove that cyclization had already occurred in the reaction system, the reaction of benzo-[*h*]quinoline N-oxide (XXIV) with methylsulfinyl carbanion was carried out in an NMR sample tube and the spectrum of the reaction mixture was measured. The results are shown in Fig. 1.

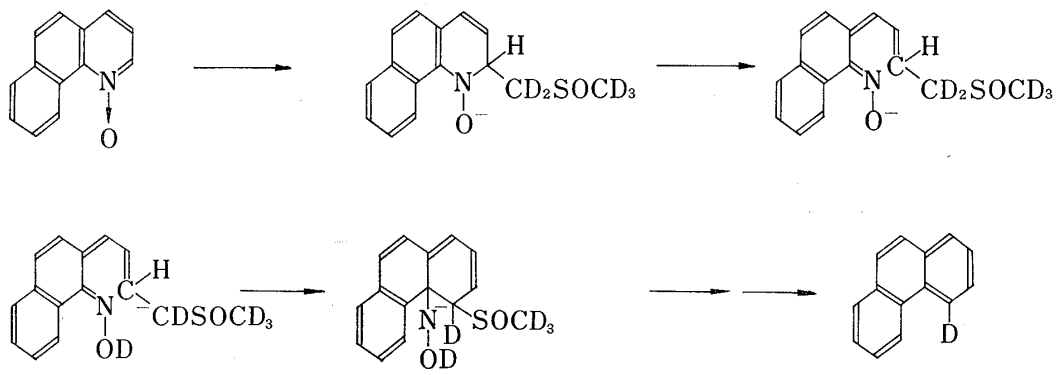

Chart 4

Compound XXIV was placed in an NMR sample tube, a solution of deuterated methylsulfinyl carbanion, formed in $(CD_3)_2SO$, as in the reaction system, was added to the sample tube under an N_2 stream, and the NMR spectrum of the reaction mixture was measured. Within 10 min, the spectrum of the starting material had disappeared and a spectrum similar to that of phenanthrene appeared. This spectral pattern and the integral ratio (1:8) of the protons on the lower field side (4- or 5-position) and the higher field side (1—3 and 6—10 positions) are very similar to those of 4-deuteriophenanthrene (XXVI). These results suggest that the mechanism shown in Chart 4 is appropriate for the liberation of the N-oxide group.

Table III. Reactivity Indices of 4,6-Phenanthrolines Calculated by the HMO Method

Compd. No.	Position of reaction	Reactivity indices		Experimental result (position)
		π-Electron density (qr)	Frontier electron density (fr^-)	
I	3	0.9044	0.0496	
	5	0.8801	0.4234	5
II	3	0.9257	0.0549	
	5	0.9696	0.3466	5
III	3	0.9597	0.0216	
	5	0.8792	0.4230	5(3.5)
IV	3	0.9597	0.0265	
	5	0.9525	0.3528	5

Parameters: $\alpha_N=\alpha+0.5\beta_0$, $\alpha_N(O)=\alpha_0+\beta_0$, $\alpha_0=\alpha_0+\beta_0$.

Consideration of Orientation by the HMO Method

To determine the reaction indices of the 3- and 5-position in 4,6-phenanthroline and its N-oxides by the HMO method, electron density and frontier electron density (fr^-) for nucleophilic substitution were calculated; the data are given in Table III.

The present experimental results indicate that the reaction occurred at the 5-position. The reaction should occur at the position with lower electron density, and calculations gave the expected results, except that the orientation was reversed in II. In the frontier electron density calculations, the reaction index was larger at the 3-position than the 5-position in all the compounds, and the results agreed well with experimental results.

Experimental

Melting points were measured with a Yanagimoto micro-melting point apparatus and are uncorrected. Proton NMR spectra were recorded using a JEOL PS-100 spectrometer with tetramethylsilane as an internal standard. The IR spectra were taken on a Jasco IR-A-1 spectrometer. Mass spectra (MS) were obtained with a Hitachi RMU-6 spectrometer operating at an ionization potential of 70 eV.

General Procedure

Method A——$CH_3SOCH_2^-$ was prepared in an N_2 atmosphere by dissolving NaH in Me_2SO. The NaH (50% mineral oil dispersion) was washed three times with absolute petroleum ether. The NaH–Me_2SO mixture was stirred vigorously at 70° until the NaH dissolved. The reaction mixture of $CH_3SOCH_2^-$ and diazaphenanthrenes or their N-oxides was stirred for 4 hr or 30 min at 70°. The reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The extract was washed with H_2O, then dried over $MgSO_4$, and the solvent was evaporated off. The residue was treated as indicated in each case.

Method B——$CH_3SOCH_2^-$ was prepared in an N_2 atmosphere by dissolving *tert*-BuOK in Me_2SO. The *tert*-BuOK–Me_2SO mixture was stirred at 70° until the *tert*-BuOK dissolved. The reaction mixture was treated by the same procedure as for method A.

5-Methyl-4,6-phenanthroline (V)——Method A: Compound I (1.71 g, 0.0095 mol) in 50 ml of Me_2SO was added to a solution of 1.32 g (0.055 mol) of NaH in 50 ml of Me_2SO at 70°, and the reaction mixture was stirred for 4 hr at 70°. The reaction mixture was treated by the same procedure as for method A. The residue was chromatographed over silica gel, and elution with benzene–$CHCl_3$ (7: 3) gave 0.85 g (46.4%) of V as white needles, mp 88—90° (from cyclohexane). *Anal.* Calcd. for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.42. Found: C, 80.14; H, 4.93; N, 14.04. MS *m/e*: 194 (M^+).

5-Methyl-4,6-phenanthroline 6-Oxide (VI)——Method B: Compound II (0.3 g, 0.0015 mol) was added to a solution of 0.95 g (0.0084 mol) of *tert*-BuOK in 50 ml of Me_2SO at 20°, and the reaction mixture was stirred for 4 hr at 20°. The reaction mixture was treated by the same procedure as for method A. The residue was chromatographed over silica gel, and elution with benzene–$CHCl_3$ (4: 1) gave 0.17 g (53.1%) of VI as white needles, mp 183—185° (from benzene–$CHCl_3$=1: 1). *Anal.* Calcd. for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.51; H, 5.01; N, 13.26. MS *m/e*: 210 (M^+), 194 (M^+-O).

N-Oxidation of V——Compound V (0.15 g) was added to a solution of 2 ml of 35% H_2O_2 and 0.1 g of Na_2WO_4, and the reaction mixture was stirred for 15 hr at 50°. After cooling, the resulting precipitate was collected and recrystallized from benzene–$CHCl_3$ (1: 1) to give 0.13 g (80.3%) of VI as white needles, mp 183—185°. MS *m/e*: 210 (M^+), 194 (M^+-O). Compound VI was identical with 5-methyl-4,6-phenanthroline 6-oxide, obtained by the methylation of II, as determined by mixed mp, and by comparison of IR and NMR spectra.

Reaction of 4,6-Phenanthroline 4-Oxide (III) with Methylsulfinyl Carbanion——Method A: Compound III (0.3 g, 0.0015 mol) in 40 ml of Me_2SO was added to a solution of 0.2 g (0.0083 mol) of NaH in 40 ml of Me_2SO at 70°, and the reaction mixture was treated by the same procedure as for method A. The residue was subjected to preparative thin-layer chromatography (TLC) [silica gel, developed with benzene–$CHCl_3$ (1: 1)] to give 8 mg (2.5%) of VII as colorless needles, mp 112—115°. MS *m/e*: 208 (M^+).

Method B: Compound II (0.3 g, 0.0015 mol) was added to a solution of 0.95 g (0.0084 mol) of *tert*-BuOK in 50 ml of Me_2SO at 20°, and the reaction mixture was treated by the same procedure as for method B. The residue was chromatographed over silica gel, and elution with benzene–$CHCl_3$ (3: 2) gave 0.15 g (38.3%) of VIII as colorless needles, mp 164—165° (from benzene). *Anal.* Calcd. for $C_{14}H_{12}N_2OS$: C, 65.60; H, 4.72; N, 10.93. Found: C, 65.45; H, 4.64; N, 10.91. MS *m/e*: 256 (M^+), 193 (M^+-SOCH_3), 179 ($M^+-CH_2SOCH_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1030 (S=O).

5-Methyl-4,6-phenanthroline 4,6-Dioxide (IX)——Method B: Compound IV (0.5 g, 0.0024 mol) was added to a solution of 1.24 g (0.011 mol) of *tert*-BuOK in 50 ml of Me_2SO at 20°, and the reaction mixture was treated by the same procedure as for method B. The residue was chromatographed over silica gel, and elution with $CHCl_3$–Me_2CO (9: 1) gave 0.12 g (22.2%) of IX as yellow needles, mp 208—210° (dec.) (from benzene). *Anal.* Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.01; H, 4.46; N, 12.38. Found: C, 69.30; H, 4.60; N, 12.51. MS *m/e*: 226 (M^+), 210 (M^+-O), 194 (M^+-20). IR ν_{max}^{KBr} cm^{-1}: 1290, 1219 (N–O).

Reaction of 1,10-Phenanthroline (X) with Methylsulfinyl Carbanion——Method A: Compound X (1.8 g, 0.01 mol) in 50 ml of Me_2SO was added to a solution of 1.32 g (0.055 mol) of NaH in 50 ml of Me_2SO at 70°, and the reaction mixture was treated by the same procedure as for method A. The residue was chromatographed over silica gel, and elution with $CHCl_3$ gave two products. The first elution gave 0.19 g (10%) of XVI as colorless needles, mp 144—145° (from cyclohexane). [At a reaction time of 30 min, 0.92 g (45%)]. *Anal.* Calcd. for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.42. Found: C, 80.32; H, 5.38; N, 14.22. MS *m/e*: 194 (M^+).

The second elution gave 0.83 g (41%) of XVII as colorless needles, mp 194—195° (from cyclohexane). [At a reaction time of 30 min, 0.12 g (6%)]. *Anal.* Calcd. for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.50; H, 5.56; N, 13.18. MS *m/e*: 208 (M^+).

Reaction of 1,7-Phenanthroline (XI) with Methylsulfinyl Carbanion——Method A: Compound XI (1.2 g, 0.0067 mol) in 50 ml of Me_2SO was added to a solution of 0.89 g (0.037 mol) of NaH in 50 ml of Me_2SO at 70°, and the reaction mixture was stirred for 30 min at 70°. The reaction mixture was treated by the same procedure as for method A. The residue was chromatographed over silica gel, and elution with $CHCl_3$ gave two products. The first elution gave 0.07 g (5%) of XVIII as colorless prisms, mp 101—102° (from petroleum ether). *Anal.* Calcd. for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.42. Found: C, 80.27; H, 5.17; N, 14.51. MS *m/e*: 194 (M^+). The second elution gave 0.3 g (18%) of XIX as a yellow gummy material. MS *m/e*: 256 (M^+), 193 (M^+-SOCH_3). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1010 (S=O). Picrate of XIX, mp 260—262° (dec.). *Anal.* Calcd. for $C_{20}H_{15}N_5O_8S$: C, 49.49; H, 3.11; N, 14.43. Found: C, 49.98; H, 3.18; N, 13.84.

Reaction of 1,10-Phenanthroline 1-Oxide (XIII) with Methylsulfinyl Carbanion——Method A: Compound XIII (0.78 g, 0.004 mol) in 10 ml of Me_2SO was added to a solution of 0.53 g (0.022 mol) of NaH in 20 ml of Me_2SO at 70°, and the reaction mixture was treated by the same procedure as for method A. The residue was chromatographed over silica gel, and elution with $CHCl_3$ gave three products. The first elution gave 0.03 g (4%) of XX as colorless needles, mp 50—52° (from cyclohexane). [At a reaction time of 30 min, 0.35 g (48%)]. *Anal.* Calcd. for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.00; H, 4.78; N, 7.56. MS *m/e*: 179 (M^+). The mp of XX was undepressed on admixture with benzo[*h*]quinoline.

The second elution was presumed to yield a mixture of XXI and XXII, 0.4 g (48%) based on the MS and NMR spectra. The mixture was chromatographed three times. The first elution gave XXI as colorless plates, mp 55—57° (from cyclohexane). MS *m/e*: 193 (M^+). The second elution gave XXII as colorless needles, mp 54—56° (from cyclohexane). The mp values of the compounds XXI and XXII was undepressed on admixture with authentic samples[4] prepared by methylation of benzo[*h*]quinoline with $CH_3SOCH_2^-$, and the identities were confirmed by comparison of their IR and NMR spectra.

The mixture of XXI and XXII is difficult to separate, and so the yield values are inaccurate. For that reason, the NMR spectrum of the mixture of XXI and XXII was measured. Based on the integral of 6-Me and 5-Me (3: 1), the yields of XXI and XXII were 36% and 12%, respectively.

Reaction of 1,7-Phenanthroline 7-Oxide (XIV) or 4,7-Phenanthroline 7-Oxide (XV) with Methylsulfinyl Carbanion——Method A: Compound XIV or XV (0.78 g, 0.004 mol) in 10 ml of Me_2SO was added to a solution of 0.53 g (0.022 mol) of NaH in 20 ml of Me_2SO at 70°, and the reaction mixture was stirred for 30 min at 70° then treated by the same procedure as for method A. The residue was chromatographed over silica gel, and elution with $CHCl_3$ gave 0.05 g (7%) of XX from XIV or 0.02 g (3%) of XXIII from XV.

XX: Colorless needles, mp 50—52° (from cyclohexane), undepressed on admixture with benzo[*h*]-quinoline. *Anal.* Calcd. for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.00; H, 4.78; N, 7.56. MS *m/e*: 179 (M^+).

XXIII: Colorless needles, mp 92—94° (for cyclohexane), undepressed on admixture with benzo[*f*]-quinoline. *Anal.* Calcd. for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.24; H, 5.15; N, 7.78. MS *m/e*: 179 (M^+).

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