have been obtained using a 4-mol excess of $BF_3 \cdot Et_2O$ and allowing the reaction to proceed for ~30 h at room temperature.

Reaction of 9 with *N*-Bromosuccinimide. A solution of **9** (0.09 g, 0.38 mmol) in dioxane–H_2O (8/2) was frozen at −30 °C and NBS (0.14 g, 0.76 mmol) was added. The reaction was then allowed to reach room temperature (4 h) and the mixture was diluted with AcOEt and washed with H_2O (2 × 50 mL), the resulting organic layer was dried (Na_2SO_4) and concentrated, and the residue was purified by preparative TLC to give 0.014 g (9.1%) of **10:** IR 1754, 1653 cm^{-1}; ^1H NMR δ 1.59 (s, 6, C_{10}–CH_3 + C_4–CH_3), 4.01 to 4.10 (m, 2, H-3 + H-6), 4.24 (t, 1, J = 3 Hz, H-9), 5.49 and 6.18 (d, 1 each, J = 3.5 Hz, C_{11}=CH_2); mass spectrum m/e (rel intensity) 404 (M^+, 1) 406 (M^+, 2), 408 (M^+, 1), 387 (1), 389 (3), 391 (1), 325 (6), 327 (8), 57 (100). Anal. Calcd for $C_{15}H_{18}{}^{79}BrO_3$: M^+ − Br, 325.0439. Found: M^+ − Br, 325.0483. Anal. Calcd for $C_{15}H_{18}{}^{81}BrO_3$: M^+ − Br, 327.0419. Found: M^+ − Br, 327.0492.

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Registry No.—**1,** 37936-58-6; **2,** 38963-61-0; **4,** 63832-99-5; **5,** 63833-00-1; **6,** 63833-01-2; **7,** 63833-02-3; **8,** 477-43-0; **9,** 63569-76-6; **10,** 63833-03-4.

References and Notes

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(11) Isoeremanthin (**9**) seems to be a powerful allergen having caused allergic contact dermatitis in some workers of this laboratory.
(12) In a similar manner **8** has been isomerized to **11** which has been converted to a compound showing similar properties with estafiatin [J. Romo, and F. Sanchez-Viesca, *Tetrahedron,* **19,** 1285 (1963)]. Estafiatin possess a 1,5-cis-fused gualane skeleton. J. Romo, private communication.
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Syntheses of Nitrogen-Containing Heterocyclic Compounds. 26.[1] Reaction of Benzo[*f* or *h*]quinolines and Their *N*-Oxides with Methylsulfinyl Carbanion

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Benzo[*h*]quinoline (**1**) and its methyl derivatives were synthesized by the modified Skraup reaction of 1-naphthylamines with glycerol, crotonaldehyde, or methyl vinyl ketone, in the presence of Sulfo-mix, ferrous sulfate, and boric acid. 1 or benzo[*f*]quinoline (**8**) was treated with dimethyl sulfoxide in the presence of sodium hydride at 70 °C to give methylated products. When benzo[*h* or *f*]quinoline *N*-oxide (**6** or **11**) was treated with methylsulfinyl carbanion in the usual procedure, a new reaction took place to produce phenanthrene (**7**) in excellent yield, whereas in the presence of potassium *tert*-butoxide only the methylated product was obtained. Reaction conditions of **6** with methylsulfinyl carbanion or deuterated methylsulfinyl carbanion and substituent effects were examined.

Reaction of quinolines, isoquinolines,[2] and their *N*-oxides[3] with methylsulfinyl carbanion has already been reported, and the products were all methylated compounds. We have also carried out methylation of 1,*X*-naphthyridines (*X* = 5, 6, 7, and 8) with methylsulfinyl carbanion.[4] In the present work, reaction of benzo[*h*]quinoline and its *N*-oxide with methylsulfinyl carbanion was carried out in order to examine the difference, if any, in reactivity between the parent ring and the *N*-oxide. We have found that the *N*-oxide and methylsulfinyl carbanion undergo an entirely different reaction.

Results and Discussion

To identify the methylated derivatives expected from methylation of benzo[*h*]quinoline, syntheses of the starting benzo[*h*]quinoline and its methylated derivatives were carried out by a modified Skraup reaction.[5] Glycerol, crotonaldehyde, and methyl vinyl ketone were reacted with 1-naphthylamine, in the presence of Sulfo-mix,[6] ferrous sulfate, and boric acid; and benzo[*h*]quinoline[7] (**1**), 2-methylbenzo[*h*]quinoline[8] (**2**), and 4-methylbenzo[*h*]quinoline[9] (**3**) were obtained in a respective yield of 50, 36, and 36%. 6-Methylbenzo[*h*]quinoline[10] (**4**) was obtained in a low yield of 15% by the application of glycerol to 4-methyl-1-naphthylamine[11] by the modified Skraup reaction. Compound **1** has been obtained by the usual Skraup reaction in 45% yield. There are several methods for the synthesis of **2,** such as the Doebner–Miller reaction of 1-naphthylamine[8a] and from acetylene and ethanol.[8b] Compound **3** has been synthesized using 1-naphthylamine and 1,3-dichloro-2,3-butene[9a] or 1-naphthylamine and ethyl acetoacetate.[9b] These synthetic methods for **2** and **3** are all complicated, and our procedure provides a better method.

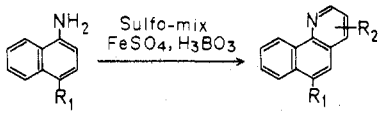
The compounds synthesized were identified by mixture melting point determination with the samples obtained by the method in the literature[7,8a,9a,10] for **1**–**4,** by comparison of IR

Table I. *S* Values[a] and the Ratios in the Lanthanide-Induced Shift of Compounds 8–10 (in $CDCl_3$)

Compd	Registry no.	Protons	H-1	H-2	H-3	H-5	H-6	H-10	5-Me	6-Me
8	85-02-9	*S* value	7.39	6.69	20.12	23.86	4.05	5.12		
		Ratio	0.31	0.28	0.84	1	0.17	0.21		
9	31486-01-8	*S* value	8.97		24.71	28.81		6.26		2.01
		Ratio	0.31		0.86	1		0.22		0.07
10	6237-04-3	*S* value	0.77		4.51		0.82	0.42	2.98	
		Ratio	0.17		1		0.18	0.09	0.66	

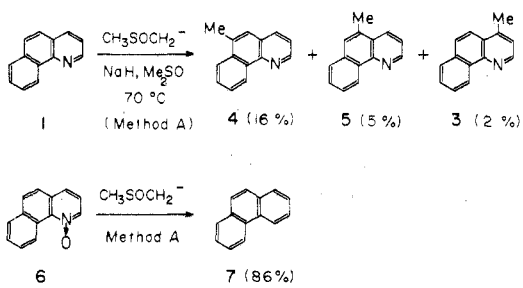
[a] *S* value = chemical shift (ppm) × [substrate]/[Eu(fod)$_3$].

Scheme I



R_1 = H, $HOCH_2CHOHCH_2OH$ 1, R_1 = H; R_2 = H (50%)
R_1 = H, $CH_3CH{=}CHCHO$ 2, R_1 = H; R_2 = 2-Me (36%)
R_1 = H, $CH_2{=}CHC(=O)CH_3$ 3, R_1 = H; R_2 = 4-Me (36%)
R_1 = Me, $HOCH_2CHOHCH_2OH$ 4, R_1 = Me; R_2 = H (15%)

Scheme II



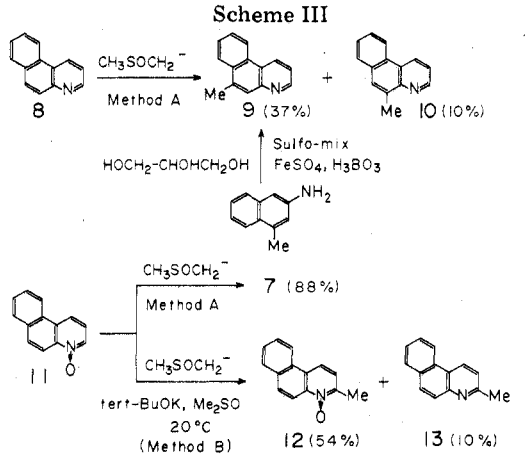
and NMR spectra. Details of these synthetic procedures are illustrated in Scheme I.

Reaction of **1** with methylsulfinyl carbanion was carried out in dimethyl sulfoxide at 70 °C for 4 h, by using sodium hydride as the base (method A), and three products were obtained: compound **4**, mp 55–57 °C; **5**, mp 54–56 °C; and **3**, mp 76–78 °C. The position of the methyl groups in these compounds was deduced from their NMR spectra, and **3** and **4** were identified by mixture melting point determination with authentic samples prepared from the Skraup reaction of 1-naphthylamine.

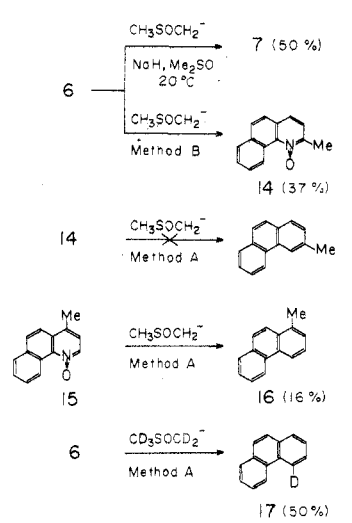
Application of methylsulfinyl carbanion to benzo[*h*]quinoline 1-oxide[12] (**6**) in dimethyl sulfoxide, by method A, gave phenanthrene (**7**) in 86% yield. Details of these reactions are illustrated Scheme II.

Kobayashi and others[3] have already carried out the reaction of benzo[*f*]quinoline and its *N*-oxide with methylsulfinyl carbanion, with sodium hydride at 20 °C for 2 h, and obtained the 5-methyl derivative from the parent compound and the 3-methyl derivative from its *N*-oxide. In order to compare benzo[*f*]quinoline (**8**) and this reaction with that of **1**, we carried out the reaction of **8** and methylsulfinyl carbanion by method A and obtained the 5-methyl compound **10** and the 6-methyl compound **9** in ca. 1:4 ratio. Compound **9** was identified by mixture melting point determination with authentic samples prepared from the Skraup reaction of 4-methyl-2-naphthylamine.[14] Compound **10** was deduced from the NMR spectra by the use of the shift reagent. The proton signals in the NMR spectrum of the 5 and 6 positions of **8** appear at around δ 7.9, there being almost no difference between them, but the addition of a shift reagent [Eu(fod)$_3$] results in lanthanide-induced shift and a difference appears between them.

Scheme III



Scheme IV



This relationship is expressed by the *S* value[13] in Table I, showing that the *S* value in **8** is greater in the proton at the 5 than at the 6 position. The *S* value of the 6 position in **10** is less than that of the 5 position in **9** and, therefore, **10** is presumed to be the 5-methylated compound.[3]

The reaction of benzo[*f*]quinoline 4-oxide[15] (**11**) with methylsulfinyl carbanion by method A gave phenanthrene in 88% yield.

The same reaction with methylsulfinyl carbanion, using potassium *tert*-butoxide as a base, at 20 °C for 4 h (method B), gave 3-methylbenzo[*f*]quinoline 4-oxide[3] (**12**), mp 123–125 °C, and a deoxygenated product, 3-methylbenzo[*f*]quinoline[16] (**13**), mp 81–82 °C. The structure of **12** and **13** was confirmed by the agreement of their melting point with those reported in literature[3,16] and from their NMR spectra. Details of these reactions are illustrated in Scheme III and their data are given in Table I.

Examination of the reaction conditions for the reaction of **6** and methylsulfinyl carbanion, as shown in Scheme IV, in-

dicated that an equal mole concentration of sodium hydride and a lower reaction temperature did not favor the formation of **7**. The use of potassium *tert*-butoxide of method B was found to inhibit liberation of the *N*-oxide group, and a product formed by methylation of the position ortho to the *N*-oxide group, 2-methylbenzo[*h*]quinoline 1-oxide (**14**), mp 128–129 °C, was obtained. This difference in reactivity of **1** and **6** with potassium *tert*-butoxide is explained by some kind of coordination of potassium ion to *N*-oxide, as reported by Kobayashi et al.[3] When the base is sodium hydride, the reaction proceeds to the formation of **7** by liberation of *N*-oxide from **6**, and we had already assumed and reported the process.[17]

An attempt to synthesize the starting **14**[18] by the N-oxidation of **2** gave the desired product in a very low yield of 5%. Therefore, **14** was prepared by the methylation of **6** with methylsulfinyl carbanion by method B. 4-Methylbenzo[*h*]-quinoline 1-oxide (**15**), mp 126–128 °C, was obtained by oxygenation of **3** with hydrogen peroxide in acetic acid. Reaction of **14** with methylsulfinyl carbanion by method A ended in recovery (50%) of the starting material, but the reaction of **15** with methylsulfinyl carbanion by method A resulted in the liberation of the *N*-oxide group, and 1-methylphenanthrene (**16**), mp 120–122 °C, was obtained.

In order to prove that the carbon from methylsulfinyl carbanion was introduced into the position vacated by liberation of the *N*-oxide group, **6** was reacted with deuterated methylsulfinyl carbanion in deuteriodimethyl sulfoxide by method A, and the reaction was stopped by the addition of water. The product **17** of mp 99–101 °C thereby obtained corresponded to formula $C_{14}H_9D$ from its elemental analytical values and mass spectrum with *m/e* 179 (M^+). It is known that the NMR spectrum of **7** exhibits the signals of equivalent C-4 H and C-5 H in a lower magnetic field than those of C-1–3 H and C-6–10 H, and their integral ratio is 2:8. In comparison of the NMR spectra of **17** and **7**, the coupling of C-4 H and C-5 H of the low-field proton signal in **17** has been unchanged, but the high-field proton signal of C-1–3 or C-6–8 in **17** has been changed. The integral ratio in the NMR spectrum of **17** for (C-4 H or C-5 H):(C-1–3 H and C-6–10 H) was 1:8.09; that is to say, one proton in the low-field proton signal has disappeared. The foregoing results indicate that **17** was to be **7** deuterated at the 4 position. Details of these reaction schemes are summarized in Scheme IV.

Conclusion

The foregoing experimental results indicate that the nucleophilic activity of **1** is the 4, 5, and 6 position from the yield of methylated products. Comparison of the nucleophilic activity of **1** and quinoline or phenanthrene indicates that the effect of the phenanthrene ring seems to be stronger than that of the ring-nitrogen atom, because of the yield of the 5- and 6-methylated products which is phenanthrene's active position more than the 4-methylated product which is quinoline's active position. Compound **8** was not methylated in 1 position, possibly due to steric hindrance, and 5- and 6-methylated compounds were obtained, indicating the activity of the phenanthrene ring.

In the reaction of **6** or **11** and methylsulfinyl carbanion, the anion was found to add to the position ortho to the *N*-oxide group, then the carbon from dimethyl sulfoxide entered the position vacated by nitrogen, followed by cyclization, and the *N*-oxide group was liberated to form **7**. This reaction is now being examined with other heterocycles.

Experimental Section

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

Benzo[*h*]quinoline (1). To a chilled (5–10 °C), homogeneous mixture of 117 g of Sulfo-mix[6] [prepared from 96 g of $H_2SO_4 \cdot SO_3$ (20%) and 21 g of nitrogenzene], 1.4 g of $FeSO_4 \cdot 7H_2O$, 2.4 g of H_3BO_3, and 25 g of anhydrous glycerol were added, followed by 11.44 g (0.08 mol) of 1-naphthylamine and 40 mL of warmed water (50 °C). The mixture was vigorously stirred in an oil bath at 130 °C for 5 h and cooled in an ice bath, and the reaction mixture was neutralized with aqueous 20% NaOH. This solution was extracted with four 100-ml portions of $CHCl_3$. The combined $CHCl_3$ extracts were washed with water, dried over $MgSO_4$, and evaporated to dryness. The solid residue was chromatographed on 100 g of alumina. The elution with C_6H_6 was recrystallized from petroleum ether to give colorless needles, mp 51–52 °C, 7.17 g (50%), of **1**, which was undepressed on admixture with an authentic sample, prepared by an earlier method,[7] and its IR spectrum was identical with that of an authentic sample.

Anal. Calcd for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.41; H, 5.35; N, 7.48.

2-Methylbenzo[*h*]quinoline (2). To a solution of 58.5 g of Sulfo-mix, 1.4 g of $FeSO_4 \cdot 7H_2O$, 2.4 g of H_3BO_3, 25 mL of water, and 5.72 g (0.04 mol) of 1-naphthylamine, warmed to 110 °C, was added dropwise over 30 min 3.5 g (0.05 mol) of crotonaldehyde. The bath temperature was raised to 130 °C, and the reaction mixture was stirred for 5 h. The cooled solution was made basic with aqueous 20% NaOH and extracted with four 100-mL portions of $CHCl_3$. The combined $CHCl_3$ extracts were washed with water, dried over $MgSO_4$, and evaporated to dryness. The brown liquid residue was chromatographed on 100 g of alumina. The elution with C_6H_6 was evaporated to give a yellow oil. Distilation gave 2.8 g (36%) of **2** as a pale-yellow liquid: bp 322–324 °C; picrate mp 224–226 °C (lit.[8a] bp 324–326 °C, picrate mp 226 °C); NMR ($CDCl_3$) δ 2.69 (s, 3, C-2 CH_3), 7.06 (d, 1, J = 8.4 Hz, C-3 H), 7.35–7.70 (m, 5, C-5 and C-9 aromatic H), 7.70 (d, 1, J = 8.4 Hz, C-4 H), 9.15 (m, 1, C-10 H); MS *m/e* 193 (M^+).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.23; H, 5.92; N, 7.06.

4-Methylbenzo[*h*]quinoline (3). The same procedure was used as for the preparation of **2**, except that 3.5 g (0.05 mol) of methyl vinyl ketone was substituted for the crotonaldehyde. Three crystallizations from cyclohexane gave colorless needles, mp 76–78 °C (lit.[9b] mp 77–78 °C), 2.8 g (36%), of **3**: NMR ($CDCl_3$) δ 2.58 (s, 3, C-4 CH_3), 7.12 (d, 1, J = 4.4 Hz, C-3 H), 7.47–7.83 (m, 5, C-5 and C-9 aromatic H), 8.64 (d, 1, J = 4.4 Hz, C-2 H), 9.14 (m, 1, C-10 H); MS *m/e* 192 (M^+).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.14; H, 5.65; N, 7.31.

6-Methylbenzo[*h*]quinoline (4). The same procedure was used as for the preparation of **1**, except that 0.63 g (0.004 mol) of 4-methyl-1-naphthylamine was substituted for the 1-naphthylamine. Three crystallizations from cyclohexane gave colorless plates, mp 55–57 °C, picrate mp 204–206 °C (lit.[11] mp 57 °C, picrate mp 206 °C), 0.12 g (15%), of **4**: NMR ($CDCl_3$) δ 2.68 (s, 3, C-6 CH_3), 7.24–7.97 (m, 5, C-5 and C-9 aromatic H), 7.33 (dd, 1, J = 8.0 Hz, C-3 H), 7.90 (dd, 1, J = 8.0 Hz, C-4 H), 8.75 (dd, 1, J = 4.4 Hz, C-2 H), 9.18 (m, 1, C-10 H); MS *m/e* 193 (M^+).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.37; H, 5.75; N, 7.18.

General Procedure of Methylsulfinyl Carbanion ($CH_3SOCH_2^-$). (A) Method A. The methylsulfinyl carbanion was prepared in a nitrogen atmosphere by dissolving sodium hydride in Me_2SO. The sodium hydride (50% mineral oil dispersion) was washed three times with absolute petroleum ether (bp 40–50 °C). The sodium hydride–Me_2SO mixture was stirred vigorously at 70 °C until the sodium hydride dissolved. The reaction mixture of methylsulfinyl carbanion was stirred for 4 h at 70 °C.

(B) Method B. The methylsulfinyl carbanion was prepared in a nitrogen atmosphere by dissolving potassium *tert*-butoxide in Me_2SO. The potassium *tert*-butoxide–Me_2SO mixture was stirred at 70 °C until the potassium *tert*-butoxide dissolved. The reaction mixture of methylsulfinyl carbanion was stirred for 4 h at 20 °C.

Reaction of 1 with Methylsulfinyl Carbanion (Method A). To a solution of 2.64 g (0.11 mol) of sodium hydride in 100 mL of Me_2SO at 70 °C was added 3.58 g (0.02 mol) of **1** in 100 mL of Me_2SO. The reaction mixture was stirred for 4 h at 70 °C under a nitrogen atmosphere followed by the addition of 100 mL of water. The reaction mixture was neutralized with aqueous 10% HCl which was extracted with four 100-mL portions of $CHCl_3$. The combined $CHCl_3$ extracts were washed with three 100-mL portions of water, dried over $MgSO_4$, and evaporated to dryness. The brown liquid residue was chromatographed three times on 200 g of silica gel. Elution with cyclohexane–benzene (10:2) gave the three kinds of products. The first elution was

recrystallized from cyclohexane to give colorless plates, mp 55–57 °C, picrate mp 204–206 °C, 0.6 g (16%), of **4**: MS *m/e* 193 (M^+).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.33; H, 5.72; N, 7.31.

The second elution was recrystallized from cyclohexane to give colorless needles, mp 54–56 °C, 0.2 g (5%), of **5**: NMR ($CDCl_3$) δ 2.62 (s, 3, C-5 CH_3), 7.41 (dd, 1, J = 8.4 Hz, C-3 H), 7.50–8.02 (m, 5, C-5 and C-9 aromatic H), 8.18 (dd, 1, J = 8.4 Hz, C-4 H), 8.93 (dd, 1, J = 4.4 Hz, C-2 H), 9.30 (m, 1, C-10 H); MS *m/e* 193 (M^+).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.12; H, 5.73; N, 7.14.

The third elution was recrystallized from cyclohexane to give colorless needles, mp 76–78 °C, 0.066 g (2%), of **3**: MS *m/e* 193 (M^+).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.19; H, 5.54; N, 7.05.

The position of the methyl group in these compounds was presumed from their NMR spectra, **5** as 5-methylbenzo[*h*]quinoline and **3** and **4**, respectively, from no depression of the melting point on mixed fusion with authentic samples prepared from the Skraup reaction of 1-naphthylamine, and by comparison of their IR and NMR spectra.

Reaction of 6 with Methylsulfinyl Carbanion. (A) Method A. To a solution of 1.06 g (0.044 mol) of sodium hydride in 40 mL of Me_2SO at 70 °C was added 1.56 g (0.008 mol) of **6** in 40 mL of Me_2SO. The reaction mixture was stirred for 4 h at 70 °C under a nitrogen atmosphere followed by the addition of 40 mL of water. The reaction mixture was neutralized with aqueous 10% HCl which was extracted with four 100-mL portions of $CHCl_3$. The combined $CHCl_3$ extracts were washed with three 100-mL portions of water, dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on 100 g of silica gel. The eluate with cyclohexane was recrystallized from petroleum ether to give colorless plates, mp 98–100 °C, 1.22 g (86%), of **8**, which was undepressed on admixture with commercial phenanthrene,[19] and its IR and NMR spectra were identical with that of phenanthrene: MS *m/e* 178 (M^+).

Anal. Calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.56; H, 5.53.

(B) The same procedure was used as for the preparation by method A, except that reaction temperature was 20 °C. **7** was prepared in 50% yield.

(C) Method B. A solution of 1.6 g (0.0143 mol) of potassium *tert*-butoxide dissolved in 25 mL of Me_2SO at 70 °C under a nitrogen atmosphere was cooled to 20 °C, and 0.5 g (0.0026 mol) of **6** was added in 25 mL of Me_2SO. The reaction mixture was stirred for 4 h at 70 °C under a nitrogen atmosphere followed by the addition 50 mL of water. The reaction mixture was neutralized with aqueous 10% HCl which was extracted with four 100-mL portions of $CHCl_3$. The combined $CHCl_3$ extracts were washed with three 100-mL portions of $CHCl_3$. The combined $CHCl_3$ extracts were washed with three 100-mL portions of water, dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on 100 g of sillica gel. The elution with $CHCl_3$ was recrystallized from C_6H_6 to give colorless needles, mp 68–70 °C, 0.2 g (37%), of **14**, which was undepressed on admixture with 2-methylbenzo[*h*]quinoline 1-oxide,[18] prepared by N-oxidation of **2**, and its IR spectrum was identical with that of an authentic sample: NMR ($CDCl_3$) δ 2.72 (s, 3, C-2 CH_3), 7.27 (d, 1, J = 8.4 Hz, C-3 H), 7.45–8.03 (m, 5, C-5 and C-9 aromatic H), 7.70 (d, 1, J = 8.4 Hz, C-4 H), 10.75 (m, 1, C-10 H); MS *m/e* 209 (M^+), 193 ($M^+ - 0$).

Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.55; H, 5.17; N, 6.31.

4-Methylbenzo[*h*]quinoline 1-Oxide (15). To a solution of 3.5 mL of acetic acid and 2.5 g of **3**, 0.7 mL of 30% H_2O_2 was added, the reaction mixture was stirred for 3 h at 110 °C and poured into 10 mL of water, and powdered MnO_2 was added. After decomposition of H_2O_2, the MnO_2 was filtered off and the filtrate was neutralized with aqueous 10% K_2CO_3, which was extracted with four 100-mL portions of $CHCl_3$. The combined $CHCl_3$ extracts were dried over $MgSO_4$ and evaporated to dryness. The residue was chromatographed on 100 g of sillica gel and eluted with C_6H_6. The first elution gave 0.3 g of starting material. The second elution was recrystallized from C_6H_6 to give colorless needles, mp 142–144 °C, 0.2 g (8%), of **15**: NMR ($CDCl_3$) δ 2.51 (s, 3, C-4 CH_3), 6.97 (d, 1, J = 6.4 Hz, C-3 H), 7.50–7.80 (m, 5, C-5 and C-9 aromatic H), 8.33 (d, 1, J = 6.4 Hz, C-2 H), 10.75 (m, 1, C-10 H); MS *m/e* 209 (M^+), 193 ($M^+ - 0$).

Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.47; H, 5.52; N, 6.58.

Reaction of 15 with Methylsulfinyl Carbanion (Method A). The same procedure was used as for the reaction of **6** with methylsulfinyl carbanion, except that 0.84 g (0.0043 mol) of **15** was substituted for **6**. The elution with cyclohexane was recyrstallized from petroleum ether to give colorelss plates, mp 120–122 °C, picrate mp 135–136 °C, 0.13 g (16%), of **16**, which was presumed from its melting point (lit.[20] mp 118 °C; picrate mp 135–136 °C) and NMR spectra to be 1-methylphenanthrene: NMR ($CDCl_3$) δ 2.64 (s, 3, C-1 CH_3), 7.20–7.85 (m, 7, C-2,3 and C-6 and C-10 aromatic H), 8.33–8.64 (m, 2, C-4 and C-5 aromatic H); MS *m/e* 192 (M^+).

Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 94.10; H, 6.12.

Reaction of 6 with Deuterated Methylsulfinyl Carbanion. The same procedure was used as for the preparation by method A, except that use of 0.2 g (0.001 mol) of **6** and Me_2SO-d_6 was substituted for the Me_2SO. The elution with cyclohexane was recrystallized from petroleum ether to give colorless plates, mp 99–101 °C, 0.09 g (50%), of **17**, which was presumed from its NMR spectrum as 4-deuteriophenanthrene: NMR ($CDCl_3$) δ 7.40–7.80 (m, 8, C-1 and C-3 and C-6 and C-10 aromatic H), 8.50 (m, 1, C-5 H); MS *m/e* (rel intensity) 180 ($M^+ + 1$, 24), 179 (M^+, 100), 178 (12), 177 (17).

Anal. Calcd for $C_{14}H_9D$: C, 93.81; H, 5.63. Found: C, 93.83; H, 5.60.

Reaction of 8 with Methylsulfinyl Carbanion (Method A). The same procedure was used as for the reaction of **1** with methylsulfinyl carbanion by method A, except that 3.4 g (0.019 mol) of **8** was substituted for **1**. The first elution was recrystallized from cyclohexane to give colorless needles, mp 81–83 °C, 0.35 g (10%), of **10**, which was presumed from its NMR spectra as 5-methylbenzo[*f*]quinoline. This melting point differs from that reported by Loader[21] (mp 100–101 °C): NMR ($CDCl_3$) δ 2.83 (s, 3, C-5 CH_3), 7.48 (dd, 1, J = 8.4 Hz, C-2 H), 7.52–7.87 (m, 3, C-7 and C-9 aromatic H), 7.77 (s, 1, C-6 H), 8.48 (m, 1, C-10 H), 8.83 (dd, 1, J = 8.4 Hz, C-1 H), 9.00 (dd, 1, J = 4.4 Hz, C-3 H); MS *m/e* 193 (M^+).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.84; H, 5.96; N, 7.02.

The second elution was recrystallized from cyclohexane to give colorless needles, mp 77–79 °C, 1.34 g (37%), of **9**, which was undepressed on admixture with 6-methylbenzo[*f*]quinoline prepared from the Skraup reaction of 4-methyl-2-naphthylamine and identified by comparison its IR and NMR spectra: NMR ($CHCl_3$) δ 2.65 (s, 3, C-6 CH_3), 7.34 (dd, 1, J = 8.4 Hz, C-2 H), 7.80 (s, 1, C-5 H), 8.03–8.52 (m, 3, C-7 and C-9 aromatic H), 8.43 (m, 1, C-10 H), 8.65 (dd, 1, J = 8.4 Hz, C-3 H); MS *m/e* 193 (M^+).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.88; H, 5.84; N, 7.10.

6-Methylbenzo[*f*]quinoline (9). The same procedure was used as for the preparation of **1**, except that 0.2 g (0.001 mol) of 4-methyl-2-naphthylamine was substituted for the 1-naphthylamine. Three crystallizations from cyclohexane gave colorless needles, mp 77–79 °C, 0.13 g (53%), of **9**: MS *m/e* 193 (M^+).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.78; H, 5.95; N, 7.06.

Reaction of 11 with Methylsulfinyl Carbanion. (A) Method A. The same procedure was used as for the reaction of **6** with methylsulfinyl carbanion by method A, except that 2.1 g (0.011 mol) of **11** was substituted for **6**. The elution was recrystallized from petroleum ether to give colorless plates, mp 98–100 °C, 1.72 g (88%), of **7**, which was undepressed on admixture with commercial phenanthrene,[19] and its IR and NMR spectra were identical with that of phenanthrene: MS *m/e* 178 (M^+).

Anal. Calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.14; H, 5.80.

(B) Method B. The same procedure was used as for the reaction of **6** with methylsulfinyl carbanion by method B, except that 1.1 g (0.0055 mol) of **11** was substituted for **6**. The first elution with C_6H_6 was recrystallized from cyclohexane to give colorless needles, mp 80–82 °C, 0.1 g (10%), of **13**, which was presumed from its melting point (lit.[21] mp 81–82 °C) and NMR spectra to be 3-methylbenzo[*f*]-quinoline: NMR ($CDCl_3$) δ 2.68 (s, 3, C-3 CH_3), 7.18 (d, 1, J = 8.4 Hz, C-2 H), 7.47–8.00 (m, 3, C-7 and C-9 aromatic H), 7.86 (s, 1, C-6 H), 7.88 (s, 1, C-5 H), 8.35 (m, 1, C-10 H), 8.55 (d, 1, J = 8.4 Hz, C-1 H); MS *m/e* 193 (M^+).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.18; H, 5.64; N, 7.40.

The second elution with $CHCl_3$–C_6H_6 (8:2) was recrystallized from cyclohexane to give pale yellow needles, mp 128–129 °C, 0.55 g (54%), of **12**, which was undepressed on admixture with 3-methylbenzo[*f*]-quinoline 4-oxide,[22] prepared by earlier method, and its IR spectrum was identical with that of an authentic sample: NMR ($CDCl_3$) δ 2.76 (s, 3, C-3 CH_3), 7.47 (d, 1, J = 9.0 Hz, C-2 H), 7.66–8.03 (m, 3, C-7 and C-9 aromatic H), 8.05 (d, 1, J = 9.4 Hz, C-6 H), 8.40 (d, 1, J = 9.0 Hz, C-1 H), 8.57 (m, 1, C-10 H), 8.82 (d, 1, J = 9.4 Hz, C-5 H); MS *m/e* 209 (M^+), 193 ($M^+ - 0$).

Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: c, 80.62; H, 5.24; N, 6.40.

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Registry No.—**1**, 230-27-3; **2**, 605-88-9; **2** picrate, 63783-90-4; **3**, 40174-37-6; **4**, 31485-96-8; **4** picrate, 63783-91-5; **5**, 59181-25-8; **6**, 17104-70-0; **7**, 85-01-8; **11**, 17104-69-7; **12**, 50697-49-9; **13**, 85-06-3; **14**, 3900-23-0; **15**, 59181-26-9; **16**, 832-69-9; **16** picrate, 63783-92-6; **17**, 62163-01-3; glycerol, 56-81-5; 1-naphthylamine, 134-32-7; crotonaldehyde, 4170-30-3; methyl vinyl ketone, 78-94-4; 4-methyl-1-naphthylamine, 4523-45-9; methylsulfinyl carbanion, 13810-16-7; dimethyl sulfoxide, 67-68-5; 4-methyl-2-naphthylamine, 4523-46-0.

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Synthesis with 1,2-Oxazines. 3.[1] Reactions of α-Chloro Aldonitrones with Enol Ethers: a Synthetic Route to Medium-Ring Lactones

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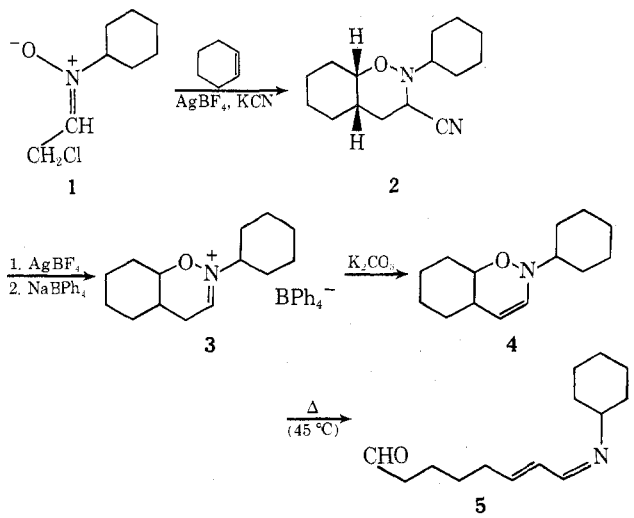
Cyclic enol ethers can undergo a Ag^+-induced cycloaddition with α-chloro nitrones. The corresponding polycyclic adducts were converted to enamoid structures of type **17b** via the immonium tetraphenylborate salts. The existence of an intramolecular ketal and the *N*-alkyl-5,6-dihydro-2*H*-1,2-oxazine ring as moieties in **17b** and **21a–c** allowed a thermolysis to the 10–12-membered lactones through cleavage of a central C–C bond in the polycyclic system. Structural effects on the thermolysis have been noted.

The usefulness of 1,4 dipolar cycloaddition for the construction of heterocyclic systems using positively charged heterodienes has been noted by some research groups.[2,3] α-Chloro nitrones were introduced by Eschenmoser as a new class of potent reagents of broad synthetic capability.[4–9] One major synthetic application of α-chloro nitrone chemistry was a new general way to construct the *N*-alkyl-5,6-dihydro-4*H*-oxazinium ion **3** in a Ag^+-induced cycloaddition reaction with isolated olefinic double bonds.[4] Imminium salts like **3** lead to a "carboxolytic" bond cleavage, occurring as a result of a retro-Diels–Alder reaction of the deprotonated enamoid derivative **4**, and end with the open-chain aldehyde **5**.



1 2 3 4 5

The object of this work was to examine if an analogous series of reactions could be applied to simple bicyclic enol ether **6** and **10a–c** (Scheme I). These were chosen as models for a possible synthesis of medium- and large-ring lactones in the α-chloro nitrone method. This involved (a) determining the generality of the cycloaddition reaction with enol ethers, (b) looking for "side" reactions and examining their influence on the cycloaddition, and (c) checking whether the carboxolytic bond cleavage procedure could also be applied in this case.

Starting enol ethers were prepared according to Obara (compound **6**)[10] and Immer (compounds **10a–c**).[11] Work on enol ethers was carried out in parallel with similar experiments on octalin (**13**) for possible special behavior in propellanes.[12] The reaction products obtained as a result of reaction with α-chloro nitrone **1** and the olefin were analyzed quantitatively and isolated by column chromatography. Results and yields are given in Table I.

The reaction products from enol ethers were mixtures of three main components: (1) cycloaddition products, (2) hydroxy ketones, and (3) a by-product having the structure **9**. Cycloaddition products were propellanes **7** and **11a–c**. It was