Reactions of *O*-Methyl *o*-Quinone Monoximes with Methyl-, Methylene- and Methine- Substituted Aromatic Compounds. Synthesis of Benzo[*d*]oxazole and 1,4-Benzoxazine derivatives

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O-Methyl *o*-quinone monoxime **1** reacts thermally with compounds **2a-d** or **6a,b** or **7a,b** to give mainly the corresponding 2-substituted phenanthroxazoles **3a-c** and **8**. The reaction of **1** with aromatic methylene compounds **10a-c** affords the ketones **13a-c** in moderate to high yields. Similar products are also obtained from the reaction of monoximes **15a,b** with some of the above reactants. The unexpected products **5** and **20** are obtained from the reaction of **1** with 2-methylimidazole (**2d**) and with phenyloxirane (**19**) respectively, while the 4*H*-1,4-oxazine derivative **23** is obtained from the reaction of **1** with indene (**21**).

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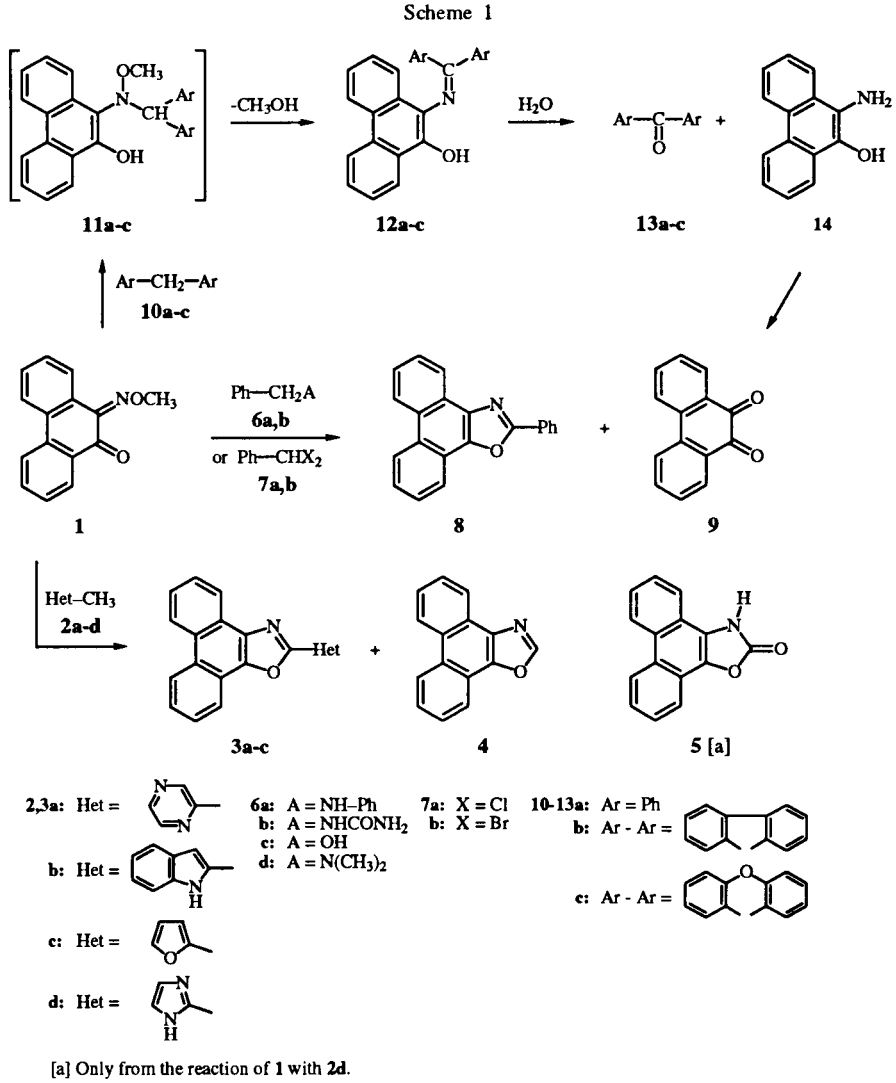
We have reported earlier [1,2] on reactions of 10-(methoxyimino)phenanthrene-9-one (**1**) with compounds Ar-CH_2-Y (Ar = aryl, heteroaryl, Y = H, OH, Br, $OCOCH_3$, SH, COR, NH_2) and with amines $PhCH_2N(CH_3)_2$, $PhNHCH_3$, $PhN(CH_3)_2$ as well as on reactions of 7-(methoxyimino)-4-methylchromene-2,8-dione [3] with similar compounds, with compounds of the type X-CH_2-COR (X = Cl, Br, R = OEt, Me, Ph) and with $PhCH_2COOCH_3$, which gave mainly the

Scheme 1



[a] Only from the reaction of **1** with **2d**.

corresponding 2-aryl-, 2-COR- and 2-amino-fused benzoxazole derivatives. The reaction of **1** with toluene in the presence of dimethyl acetylenedicarboxylate afforded in addition to 2-phenylphenanthro[9,10-*d*]oxazole (**8**) dimethyl 2-phenyldibenzo[*f,h*]quinoline-3,4-dicarboxylate, through the trapping by the dienophile of a 2-aza-1,3-heterodiene intermediate. Very recently [4] we also found that the reaction of **1** with several aryl acetates gives the corresponding 3-aryl-2*H*-phenanthro[9,10-*b*][1,4]oxazin-2-ones as well as phenanthro-[9,10-*d*]oxazole (**4**) and the corresponding substituted compounds **8**. The reaction of monoximes **1** and **15a,b** with *trans*-stilbene gives initially the expected Diels-Alder products.

In order to investigate further the reactivity of the previously studied monoximes we present this paper. In this work the reactions of the *O*-methyl *o*-quinone monoximes **1** and **15a,b** with different alkyl substituted aromatic compounds are involved, as depicted in Schemes 1-4.

The products obtained from the reaction of monoxime **1** with methylheteroaryl derivatives **2a-d**, with methylene derivatives **6a,b** and **10a-c** with methine derivatives **7a,b** and are summarized in Scheme 1 and Table 1. The products obtained from some similar reactions of monoximes **15a,b** are also summarized in Scheme 2 and in Table 1, where the temperature and the reaction time for each experiment are also given. The liquid substrates which were used in excess served furthermore as solvents. The solid substrates, used also in excess, were melted with monoximes. The only exception was the reaction of compounds **2b,d**, which were used in equimolecular amounts with the substrates. All the reaction mixtures were separated by column chromatography on silica gel.

The reaction of **1** with methyl heteroaromatic derivatives **2a-c** gave the expected [1,2] 2-heterocyclic-substituted oxazoles **3a-c** as well as compounds **4** and **9** (Table 1). Compound **4** was also obtained from several other reactions of **1** reported previously [1,2]. The reaction of **1** with 2-methylimidazole (**2d**) afforded compound **4** (39%) along with the known [5] compound **5** in 37% yield. The expected compound **3d** was not isolated or detected in the reaction mixture. Compound **5** can be considered as the hydrolysis product of **3d** with analytical and spectral data in good agreement with the proposed structure.

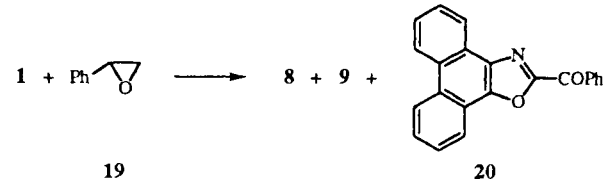
Table 1

Experimental Data for the Reaction of the Methoxyimino Compounds **1** and **15a,b** with Alkyl Substituted Compounds **2a-d, 6a-c, 7a,b** and **10a-c**

Methoxyimino Compound	Alkyl Substituted Compound	Temperature °C	Reaction Time	Products Obtained (%)
1	**2a**	135	8 hours	**3a** (13), **9** (43)
1	**2b**	170	20 minutes	**3b** (13)
1	**2c**	65	9 hours	**3c** (11), **4** (7)
1	**2d**	150	2.5 hours	**4** (39), **5** (37)
1	**6a**	150	30 minutes	**8** (46)
1	**6b**	150	2.5 hours	**8** (47)
1	**7a**	150	3 days	**8** (11), **9** (35)
1	**7b**	150	3.5 hours	**8** (10), **9** (60)
1	**10a**	150	5 hours	**9** (38), **13a** (29)
1	**10b**	150	10 minutes	**9** (27), **13b** (82)
1	**10c**	150	10 minutes	**9** (67), **13c** (57)
15a	**10c**	150*	10 minutes	**16a** (42), **13c** (50)
15a	**6c**	150	18 hours	**17a** (61)
15a	**6d**	150	1 hour	**17a** (23), **18** (26)
15a	**7a**	150	3 days	**17a** (51)
15b	**10c**	150*	10 minutes	**13c** (44)
15b	**6c**	150	20 minutes	**17b** (13)

* Melted.

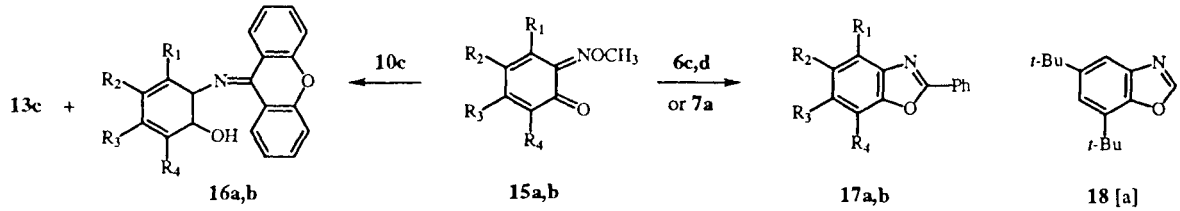
Scheme 3



19 **20**

The reaction of **1** with excess of the benzyl derivatives **6a** and **6b** afforded compound **8** in 46% and 47% yield, respectively, as reported earlier [2] for the similar reaction of **1** with compounds Ar-CH_2-Y. Possibly, the formation of an intermediate analogous to **11**, but carrying a substituent -N(OCH_3)-CHAPh instead of -N(OCH_3)$CHAr_2$, followed by intramolecular eliminations of AH and methanol can account for the formation of compound **8**. More evidence is necessary to explain the formation of compound **8**, also obtained in lower yield along with phenanthrene-9,10-

Scheme 2



16a,b **15a,b** **17a,b** **18** [a]

15-17a: $R_1 = R_3 = H$, $R_2 = R_4 = t$-Bu
b: $R_1 - R_2 = R_4 - R_3 =$ -N=CH-CH=CH-

[a] Only from the reaction of **15a** with **6d**.

quinone (**9**) from the reaction of **1** with dihalo derivatives **7a,b**. Most probably, the initial formation of an intermediate similar to **11** having the substituent -N(OCH$_3$)CX$_2$Ph is followed by dihydrooxazole ring closure through intramolecular elimination of HX. Further intermolecular interactions with other reactive species present, leading to elimination of the MeO and X substituents can account for the final formation of the oxazole ring.

Treatment of monoxime **1** with compounds **10a-c** afforded in moderate to high yields the corresponding ketones **13a-c** and quinone **9**. Similarly, the reaction of xanthene (**10c**) with monoxime **15b** gave xanthone (**13c**) in 44% yield, while the reaction between **10c** and monoxime **15a** gave mainly the imine **16a** (42%) along with ketone **13c** (50%) (Scheme 2). Obviously, ketones **13a-c** obtained from these reactions are formed through the further hydrolysis of the imine intermediates **12a-c** and **16a,b**, respectively, as it was confirmed by a controlled hydrolysis of **16a** to **13c** with tlc examination of the reaction mixture. The formation of similar imine intermediates from other reactions of the title monoximes, leading finally to 2-substituted fused oxazoles has been also suggested previously [1]. The expected *o*-aminophenol **14** from the hydrolysis of the intermediates **12a-c** is further air oxidized [6] to the isolated *o*-quinone **9**, while the also expected *o*-aminophenol derivatives from the hydrolysis of **16a,b** were not obtained, most probably because they are moderately unstable in air [7]. MO calculations of the relative thermodynamic stabilities of compounds **12c** and **16a** *versus* their tautomeric *o*-quinone imine by the AM1 method [8] confirm that the *o*-hydroxy aromatic Schiff base is favored by 11.2 kcal/mol for **12c** and by 24.6 kcal/mol for **16a**, in agreement with a previously reported [9] MNDO calculation for analogous tautomerization, leading by further hydrolysis to *o*-aminophenol derivatives mentioned above.

Corey and Achiwa found [10] that the 3,5-di-*tert*-butyl-1,2-benzoquinone efficiently converted *sec*-alkyl primary amines to ketones *via* the hydrolysis of intermediate Schiff bases similar to **16a**. In the case of the unbranched primary amines the intermediate in question gave benzoxazoles similar to **17**. This oxidation was suggested [11] to be mediated by the quinone present and not by oxygen. On the other hand, the transformation of the intermediates **12a-c** and **16a,b** into dihydrobenzoxazoles does not proceed, because the elimination of the AH moiety in this stage is not possible, in accordance with our previous observations [1-4]. Most probably the reaction studied by Corey and that described above proceed through similar mechanisms.

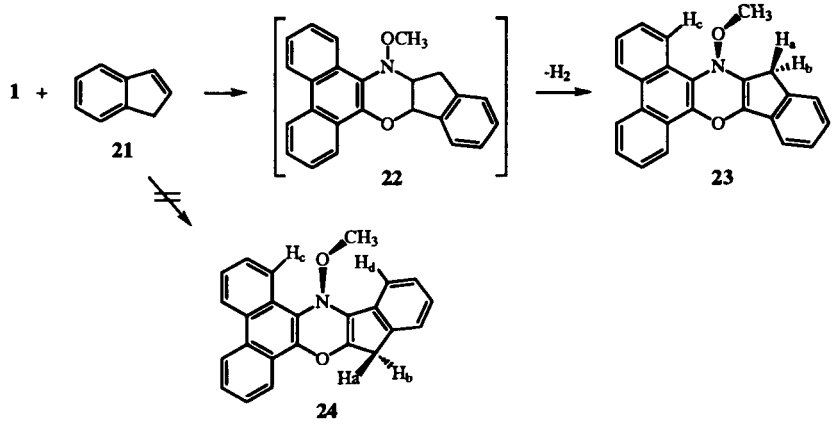
We further investigated the reaction of **1** with phenyloxirane (**19**) and indene (**21**), which can be considered as methine and methylene aryl derivatives, respectively. The reaction of **1** with **19** gave compound **8** (22%), quinone **9** (16%) and the known [12] compound **20** (7%). The spectral data of an authentic sample of compound **20** prepared according to the literature [12] were identical with those of the product in question. Obviously, two different reaction mechanisms proceed for the formation of the above 2-substituted oxazole derivatives **8** and **20** and more evidence is necessary to explain explicitly the formation of these two unexpected products.

The reaction of compound **1** with indene afforded the fused 4*H*-oxazine derivative **23** in 15% yield, *via* a Diels-Alder cycloaddition of the dienophile to the 1,4-oxaaza-1,3-diene moiety of **1** and further oxidation by air. The mass spectrum of the product gave correct molecular ion, the ^{1}H nmr spectrum exhibited two AB doublets at δ = 3.39 (J = 18 Hz) and at δ = 3.85 (J = 18 Hz) and the ^{13}C nmr showed the presence of the methylene carbon atom at δ = 38.49. The distinction between the two possible *regio*-isomers **23** and **24** has been made by NOE Difference Spectroscopy. By irradiation of the methoxy protons at 3.29 ppm a +10% NOE for the doublet at 3.85 ppm, a +10% for the doublet at 3.39 ppm and a +2% for the multiplet at 8.54 ppm was measured. A molecular modeling study [13] on compounds **23** and **24** showed that the methoxy group is in a crowded area with restricted rotation about N-O bond. As a consequence, H_a shows a positive NOE and a downfield deshielding effect, but H_b shows a negative NOE. At the aromatic protons region the positive NOE is assigned to the H_c. The above data are in accordance with structure **23**, while structure **24** would show two aromatic protons (H_c and H_d) with positive NOE. In addition, the distance between the methylene proton H_a and the methyl protons in compound **23** is ~ 2.9 Å, while in compound **24** ~ 5.0 Å. This long distance from the center of asymmetry in compound **24** would not explain the AB pattern of methylene group and the NOE values obtained. AM1 MO calculations carried out on the above Diels-Alder addition showed [14] also a preference on the formation of compound **23** over **24**.

A similar *regio*-selectivity has also been proposed in the case of the reactions of compound **1** with 1,1-bis(*p-N,N*-dimethylaminophenyl)ethylene and 1,1-bis(*p-N,N*-dimethylaminophenyl)-2-methylene, which afforded the corresponding 2,2-diaryl-2*H*-1,4-oxazines *via* Diels-Alder cycloaddition and further dehydration [15]. It is worth to be noticed that the reaction of **1** with dimethyl acetylenedicarboxylate in dioxane afforded dimethyl 7-oxo-7*H*-dibenzo[*de,g*]quinoline-4,5-dicarboxylate *via* an unusual [4+2] cycloaddition of the dienophile across the heterodiene system -C=C-C=N-OCH$_3$ of **1** extended from the exocyclic imino bond to the aromatic system followed by methanol elimination [1].

The described reaction of the title monoximes with compounds **10a-c** can serve as a method for the conversion of the latter to ketones in neutral media.

Scheme 4



EXPERIMENTAL

General.

Melting points (mp) were determined on a Kofler hot-stage apparatus and are uncorrected.The ir spectra were obtained with a Perkin-Elmer 297 spectrophotometer as Nujol mulls and are reported in wavenumbers (cm^{-1}). The ^1H nmr spectra were recorded on a Bruker AW 80 (80 MHz) or on a Bruker AM-300 (300 MHz) spectrometer, where it is indicated and ^{13}C nmr spectra were obtained at 75 MHz all as deuteriochloroform solutions. Chemical shifts for ^1H and ^{13}C nmr spectra are reported in ppm downfield relative to internal tetramethylsilane. Mass spectra were determined on a VG TS-250 double focusing spectrometer in the EI mode (70 eV). Elemental microanalyses were performed with a Perkin-Elmer model 240B CHN analyzer. Light petroleum used as an eluent refers to the fraction of 40-60°.

All computations were carried out on a VAX Station 2000 using the MOPAC package [16] *version 6*. The geometries of the molecules were fully optimized by minimizing the energy with respect to all internal coordinates except for the substituent CH_3 where some symmetry was taken into account (equal bond lengths for C-H bonds).

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with 2-Methylpyrazine (**2a**). Preparation of 2-(2'-Pyrazinyl)phenanthro-[9,10-*d*]oxazole (**3a**).

A solution of **1** (0.400 g, 1.69 mmoles) in **2a** (2 ml) was refluxed for 8 hours and then column chromatographed on silica gel to afford phenanthrene-9,10-quinone (**9**), (0.150 g, 43%) and **3a**, (65 mg, 13%), mp 250-253° (from ethanol); ^1H nmr (deuteriochloroform): δ 7.50-8.01 (m, 4H), 8.29-8.55 (m, 2H), 8.57-8.87 (m, 4H), 9.66 (s, 1H); ms: m/z (%) 297 ($M^{+\cdot}$, 100), 269 (3), 245 (7), 235 (13).

Anal. Calcd. for $C_{19}H_{11}N_3O$: C, 76.76; H, 3,73; N, 14.13. Found: C, 76.81; H, 4.01; N, 14.31.

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with 2-Methylindole (**2b**). Preparation of 2-(2'-Indolyl)-phenanthro-[9,10-*d*]oxazole (**3b**).

A mixture of **1** (0.300 g, 1.26 mmoles) and **2b** (0.200 g, 1.52 mmoles) was heated at 170° for 20 minutes. Column chromatography on silica gel with light petroleum-ethyl acetate (15:1) afforded **3b** (55 mg, 13%), mp 221-222° (from ethanol-methylene chloride); ir: 3340, 1605 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.20-7.80 (m, 9H), 8.35-8.78 (m, 4H), 9.38 (br. s, 1H); ms: m/z (%) 334 ($M^{+\cdot}$, 100), 305 (17), 164 (15), 163 (20).

Anal. Calcd. for $C_{23}H_{14}N_2O$: C, 82.62; H, 4.22; N, 8.38. Found: C, 82.68; H, 3.81; N, 8.31.

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with 2-Methylfuran (**2c**). Preparation of 2-(2'-Furyl)phenanthro[9,10-*d*]-oxazole (**3c**).

A solution of **1** (0.400 g, 1.69 mmoles) in **2c** (3 ml) was refluxed for 9 hours and then column chromatographed on silica gel (light petroleum-ethyl acetate 10:1) to afford **3c**, (53 mg, 11%), mp 81-83° (from ether-light petroleum); ir: 1615 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.15-7.85 (m, 6H), 8.10-8.40 (m, 2H), 8.42-8.85 (m, 3H); ms: m/z (%) 285 ($M^{+\cdot}$, 24), 220 (55), 219 (36), 191 (26), 190 (44), 164 (88), 163 (100).

Anal. Calcd. for $C_{19}H_{11}NO_2$: C, 79.99; H, 3.89; N, 4.91. Found: C, 80.29; H, 4.11; N, 4.86.

Compound phenanthro[9,10-*d*]oxazole (**4**), (27 mg, 7%) was eluted next.

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with 2-Methylimidazole (**2d**). Preparation of Phenanthro[9,10-*d*]oxazole (**4**) and 2,3-Dihydrophenanthro[9,10-*d*]oxazole-2-one (**5**).

A mixture of **1** (0.400 g, 1.69 mmoles) and **2d** (0.138 g, 1.68 mmoles) was heated for 2.5 hours at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate 7:1) to afford **4**, (0.145 g, 39%), mp 144-146° (from ethanol) (lit [1] mp 143-146°). Compound **5** was eluted next (0.148 g, 37%), mp 302-305° (from ethanol) (lit [11] mp 305-307°); ^1H nmr (deuteriochloroform): δ 7.49-7.74 (m, 4H), 8.05-8.22 (m, 2H), 8.38-8.76 (m, 3H); ms: m/z (%) 235 ($M^{+\cdot}$, 100), 180 (39), 179 (66), 177 (25), 152 (19), 151 (25).

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with *N*-Phenylbenzylamine (**6a**).

A mixture of **1** (0.237 g, 1 mmole) and **6a** (0.366 g, 2 mmoles) was heated for 30 minutes at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate 20:1) to afford compound 2-phenylphenanthro[9,10-*d*]oxazole (**8**) (0.137 g, 46%), mp 204-205° (from methylene chloride-light petroleum) (lit [1] mp 204-205°).

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with Benzylurea (**6b**).

A mixture of **1** (0.237 g, 1 mmole) and **6b** (0.300 g, 2 mmoles) was heated for 2.5 hours at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate 20:1) to afford compound **8** (0.140 g, 47%).

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with α,α-Dichlorotoluene (**7a**).

A solution of **1** (0.25 g, 1.05 mmoles) in **7a** (1 ml) was heated for 3 days at 150° and then column chromatographed on silica gel (light petroleum-methylene chloride 4:1 up to 2:1) to afford compound **8** (33 mg, 11%) and compound **9** (77 mg, 35%).

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with α,α-Dibromotoluene (**7b**).

A solution of **1** (0.237 g, 1 mmole) in **7b** (0.5 ml) was heated for 3.5 hours at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate 1:0 up to 1:1) to afford compound **8** (30 mg, 10%) and compound **9** (0.124 g, 60%).

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with Diphenylmethane (**10a**).

A mixture of **1** (0.250 g, 1.04 mmoles) and **10a** (1.0 g, 5.9 mmoles) was heated for 5 hours at 150° and then column chromatographed on silica gel (light petroleum-methylene chloride 3:1) to afford first compound **13a** (55 mg, 29%) and second compound **9** (82 mg, 38%).

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with Fluorene (**10b**).

A mixture of 10-(Methoxyimino)phenanthren-9-one (**1**) (0.237 g, 1 mmole) and **10b** (0.498 g, 3 mmoles) was heated for 10 minutes at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate 30:1 up to 2:1) to afford first 9-fluorenone (**13b**) (0.147 g, 82%), mp 83-85°; the next fraction gave compound **9** (57 mg, 27%).

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with Xanthene (**10c**).

A mixture of **1** (0.213 g, 0.9 mmole) and **10c** (0.546 g, 3 mmoles) was heated for 10 minutes at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate 30:1 up to 10:1) to afford first xanthone (**13c**) (0.100 g, 57%), mp 174-176°; the next fraction gave compound **9** (0.125 g, 67%).

Reaction of 2-Methoxyimino-4,6-di-*tert*-butylbenzen-1-one (**15a**) with Xanthene (**10c**). Preparation of Compound **16a**.

A mixture of **15a** (lit [17]) (0.100 g, 0.4 mmole) and **10c** (0.219 g, 1.2 mmoles) was heated for 10 minutes at 150° and then column chromatographed on silica gel (light petroleum-dichloromethane 1:0 up to 0:1) to afford first the imine **16a** (67 mg, 42%) oil; ir: 3478, 1709, 1590 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.15 (s, 9H), 1.46 (s, 9H), 6.67 (s, 1 H), 6.80-7.89 (m, 10H); ms: m/z (%) 399 ($M^{+\cdot}$, 100), 384 (63), 368 (9), 357 (18), 342 (15), 196 (8), 181 (90), 152 (8).

Anal. Calcd. for $C_{27}H_{29}NO_2$: C, 81.17; H, 7.32; N, 3.51. Found: C, 81.00; H, 7.20; N, 3.39.

Compound **13c** (39 mg, 50%) was eluted next.

Preparation of 6-Methoxyimino[4,7]phenanthrolin-5-one (**15b**).

A solution of 4,7-phenanthroline-5,6-dione (2.1 g, 10 mmoles) and methoxyamine hydrochloride (0.835 g, 10 mmoles) in methanol (73 ml) was refluxed for 30 minutes. Compound **15b** precipitated on cooling (1.92 g, 80%), mp 213-215° (from methanol); ir: 1680, 1607 cm^{-1}; ms: m/z (%) 239 ($M^{+\cdot}$, 24), 211 (18), 180 (100), 153 (15), 126 (15).

Anal. Calcd. for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.57. Found: C, 65.30; H, 3.58; N, 17.30.

Reaction of 6-Methoxyimino[4,7]phenanthrolin-5-one (**15b**) with Xanthene (**10c**).

A mixture of **15b** (0.100 g, 0.418 mmole) and **10c** (0.228, 1.25 mmoles) was heated for 10 minutes at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate-methanol 5:1:0 up to 0:1:3) to afford compound **13c** (36 mg, 44%).

Reaction of 2-Methoxyimino-4,6-di-*tert*-butylbenzene-1-one (**15a**) with Benzylalcohol (**6c**).

A solution of **15a** (0.249 g, 1 mmole) in **6c** (1 ml) was heated for 18 hours at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate 18:1) to afford **17a** (0.187 g, 61%), oil (lit [18]); ^1H nmr (deuteriochloroform): δ 1.37 (s, 9H), 1.54 (s, 9H), 7.25-7.76 (m, 5H), 8.12-8.38 (m, 2H); ms: m/z (%) 307 ($M^{+\cdot}$, 69), 292 (100), 237 (24), 198 (5).

Reaction of 2-Methoxyimino-4,6-di-*tert*-butylbenzen-1-one (**15a**) with *N,N*-Dimethylbenzylamine (**6d**).

A solution of **15a** (0.249 g, 1 mmole) in **6d** (1 ml) was heated for 1 hour at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate 1:0 up to 1:1) to afford first compound **17a** (71 mg, 23%) and next **18** (61 mg, 26%), oil (lit [19] mp 54°); ir: 1607 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.36 (s, 9H), 1.47 (s, 9H), 7.33 (br s, 1H), 7.66 (br s, 1H), 8.04 (s, 1H); ms: m/z (%) 231 ($M^{+\cdot}$, 29), 217 (100), 201 (30), 189 (21), 115 (20).

Reaction of 2-Methoxyimino-4,6-di-*tert*-butylbenzen-1-one (**15a**) with α,α-Dichlorotoluene (**7a**).

A solution of **15a** (0.249 mg, 1 mmole) in **7a** (1 ml) was heated for 3 days at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate 20:1 up to 10:1) to afford **17a** (0.157 g, 51%).

Reaction of 6-Methoxyimino[4,7]phenanthrolin-5-one (**15b**) with Benzyl Alcohol (**6c**). Preparation of 2-Phenyl[4,7]phenanthrolino[5,6-*d*]oxazole (**17b**).

A solution of **15b** (0.239 g, 1 mmole) in **6c** (1 ml) was heated for 20 minutes at 150° and then column chromatographed on silica gel (ethyl acetate-ethanol 2:1 up to 0:1) to afford **17b** (39 mg, 13%), mp 269-270° (from methylene chloride-ethyl acetate); ir: 1620 cm^{-1}; ^1H nmr (300 MHz) (deuteriochloroform): δ 7.51-7.70 (m, 3H), 7.95-8.12 (m, 3H), 8.52-8.68 (m, 3H), 9.00-9.10 (m, 2H); ms: m/z (%) 297 ($M^{+\cdot}$, 30), 296 (100), 85 (9).

Anal. Calcd. for $C_{19}H_{11}N_3O$: C, 76.76; H, 3.73; N, 14.13. Found: C, 76.68; H, 3.76; N, 13.92.

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with Phenyloxirane (**19**). Preparation of 2-Benzoylphenanthro[9,10-*d*]-oxazole (**20**).

A mixture of **1** (0.237 g, 1 mmole) and **19** (0.420 g, 3.5 mmoles) was heated for 1 hour at 150° and then column chromatographed on silica gel (light petroleum-ethyl acetate 20:1 up to 3:1) to afford

first compound **8** (65 mg, 22%) and second compound **20** (23 mg, 7%), mp 200-202° (from ethanol) (lit [12] 201-203°); ir: 1665 cm^{-1}. Quinone **9** (33 mg, 16%) was eluted next.

Reaction of 10-(Methoxyimino)phenanthren-9-one (**1**) with Indene (**21**). Preparation of Compound **23**.

A solution of **1** (0.237 g, 1 mmole) in **21** (0.5 ml) was heated for 30 minutes at 150° and then column chromatographed on silica gel (light petroleum-methylene chloride 1:1) to afford compound **23** (52 mg, 15%), mp 208-213° (from methylene chloride-methanol); ir: 1630, 1600 cm^{-1}; ^1H nmr (300 MHz, deuteriochloroform): δ 3.28 (s, 3H), 3.37 (d, AB J = 16.4 Hz, 1H), 3.84 (d, AB J = 16.4 Hz, 1H), 7.44-7.55 (m, 3H), 7.62-7.75 (m, 4H), 8.16 (d, J = 7.3 Hz, 1H), 8.52-8.55 (m, 1H), 8.65 (d, J = 8.1 Hz, 1H), 8.69-8.72 (m, 1H), 8.91 (d, J = 8.1 Hz, 1H); ^{13}C nmr (75 MHz, deuteriochloroform): δ 160.6, 144.0, 135.7, 135.5, 132.3, 130.6, 130.0, 128.1, 127.3, 127.2, 127.0, 126.8, 126.1, 125.5, 125.4 [20], 125.2, 124.0, 123.5, 122.9, 122.4, 122.2, 97.6, 49.9, 38.5; ms: m/z (%) 351 ($M^{+\cdot}$, 75), 336 (43), 321 (43), 320 (100), 319 (47), 308 (89), 291 (17), 290 (24), 279 (8), 278 (11), 252 (15), 230 (29), 190 (11), 176 (17), 163 (28).

Anal. Calcd. for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.21; H, 4.99; N, 4.12.

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