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Dedicated to the memory of Professor Nicholas Alexandrou

10-(Methoxyimino)phenanthrene-9-one **1** reacts thermally with the arylacetic derivatives **2(a-j)** to yield the corresponding 1,4-benzoxazin-2-ones **4(a-d,f)** and benzo[*d*]oxazoles **5(a-e,g)**. Similarly, reaction of the monoximes **7a**, **7b** with compounds **2a**, **2d** respectively affords **8a**, **8b**, while action of *trans*-stilbene on the monoximes **1**, **7a**, **7b** leads to the 1,4-benzoxazines **10**, **11**, **13**, obtained along with the corresponding 2-phenyloxazoles **5a**, **8a**, **8c** and compound **12**.

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As we already [1,2] reported, 10-(methoxyimino)-phenanthrene-9-one **1** reacts thermally with compounds Ar-CH₂-Y (Ar = aryl, heteroaryl, Y = H, Br, OH, OCOCH₃, CPh, SH, COCH₃, NH₂) to yield the corresponding 2-aryl-phenanthro[9,10-*d*]oxazoles **5** and/or the parent compound **6**. On the same pattern, treatment of compound **1** with the amines PhCH₂N(CH₃)₂, PhN(CH₃)₂ and PhNHCH₃ affords the 2-amino substituted oxazoles **5** [Ar = N(CH₃)CH₂Ph, N(CH₃)Ph, NHPPh] along with the forementioned oxazole **6**. We further [3] found out that 7-(methoxyimino)-4-methylchromene-2,8-dione reacts with compounds of the types Ar-CH₂-Y [Y = H, Cl, COOCH₃, N(CH₃)₂] and X-CH₂-COR (X = Cl, Br, R = OC₂H₅, CH₃, Ph) to give the corresponding 2-Ar- and 2-COR-1-8*H*-pyrano[3,2]benzoxazol-8-ones along with the unsubstituted parent compound. Reaction [4] of the monoxime **1** with phosphorus ylides leads to similar 2-substituted oxazolocoumarins instead of the Wittig products expected [5,6], while action of *N*-methylaniline affords high yields of 7-amino-8-hydroxy-4-methylcoumarin. The work detailed at present involves interaction of the title 2-(methoxyimino)benzen-1-ones **1** and **7(a,b)** with the arylacetates **2(a-f)**, the arylacetic acids **2(g-j)** and *trans*-stilbene **9**, leading to the title 1,4-benzoxazin-2-ones, benzo[*d*]oxazoles and 1,4-benzoxazines, as depicted in Schemes 1-3.

The products obtained from the reaction of compound **1** with the arylacetic acid derivatives **2(a-j)** are summarized in Scheme 1 and Table 1. All procedures took place at 190° and for periods varying from 10 to 105 minutes. The reactants **2(a,b,d-f,j)** being liquid, they served furthermore as solvents, while **2(c,g-i)** were melted with equimolecular amounts of the monoxime **1**. The reaction mixtures were separated chromatographically.

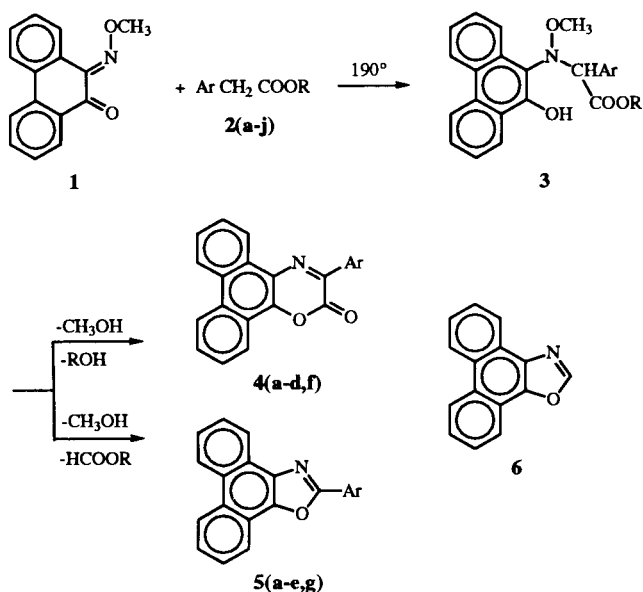
As seen in Scheme 1 and Table 1, treatment of compound **1** with the esters **2(a-f)** affords the corresponding 3-aryl-2*H*-phenanthro[9,10-*b*][1,4]oxazin-2-ones **4(a-d,f)** in yields reaching 29%, as well as the 2-aryl-phenanthro-

Table 1
Experimental Data for the Action of the Arylacetic Acid Derivatives **2(a-j)** on the Methoxyimino Compounds **1**, **7(a,b)**

<i>N</i> -Methoxyimino Compound	Arylacetic Acid Derivative	Reaction Time (min)	Products obtained (%)
1	2a	35	4a (25), 5a (10)
1	2b	40	4b (25), 5b (11)
1	2c	30	4c (4), 5c (18)
1	2d	40	4d (28), 5d (5)
1	2e	105	5e (17)
1	2f	10	4f (29)
1	2g	60	4d (6), 5d (15)
1	2h	15	5e (22)
1	2i	10	4f (1.5), 6 (14)
1	2j	25	5g (19)
7a	2a	330	8a (17)
7b	2d	60	8b (43)

[9,10-*d*]oxazoles **5(a-e,g)** in 5-22% yield. Action of the arylacetic acids **2(g-j)** on **1** leads to lower yields, while the parent compound **6** and a small amount (8%) of phenanthrene-9,10-quinone are also obtained from **2i**. The structures proposed fully agree with the analytical and spectroscopic data of the products. It should be mentioned that compounds **4**, **5** and **6** possess a rather intense fluorescence. In analogy to a mechanism we already proposed [1,2], the oxazole derivatives **5** are probably due to free radical formation of the intermediate **3** and further homolytic elimination of methanol and formic acid/formates from the latter. Alcohol elimination and subsequent lactonization of **3** leads to the oxazin-2-ones **4**. It may be assumed that compounds of the oxazole type derived from both geometrical isomers of the imines formed *via* methanol elimination from the intermediate **3**, while the oxazin-2-ones can only be due to the *Z*-isomer. Further evidence is necessary to explain the presence of the unsubstituted oxazole **6**. Scheme 2 and Table 1 summarize the products obtained from the monoximes **7(a,b)** when reacting with the esters **2(a,d)**. The reaction conditions are similar to those of Scheme 1.

Scheme 1

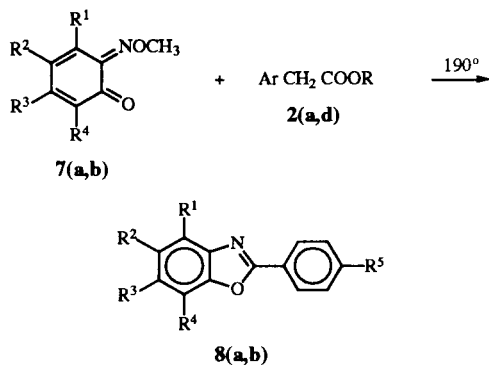


- 2,3a, Ar = C₆H₅, R = CH₃
 b, Ar = 4-CH₃-C₆H₄, R = C₂H₅
 c, Ar = 4-NO₂-C₆H₄, R = C₂H₅
 d, Ar = 4-CH₃O-C₆H₄, R = CH₃
 e, Ar = 2-naphthyl, R = C₂H₅
 f, Ar = 3-pyridyl, R = C₂H₅
 g, Ar = 4-CH₃O-C₆H₄, R = H
 h, Ar = 2-naphthyl, R = H
 i, Ar = 3-pyridyl, R = H
 j, Ar = 4-HO-C₆H₄, R = H

- 4,5a, Ar = C₆H₅
 b, Ar = 4-CH₃-C₆H₄
 c, Ar = 4-NO₂-C₆H₄
 d, Ar = 4-CH₃O-C₆H₄
 e, Ar = 2-naphthyl
 f, Ar = 3-pyridyl
 g, Ar = 4-HO-C₆H₄

Treatment of 2-(methoxyimino)-4,6-di-*t*-butylbenzen-1-one **7a** with the ester **2a** for 5.5 hours at 190°, followed by column chromatographic separation of the reaction mixture leads to 17% of the known oxazole **8a**, while reaction of 6-(methoxyimino)[4,7]phenanthrolin-5-one **7b** with the ester **2d** gives as well 43% of 2-(4-methoxyphenyl)-[4,7]phenanthroline[5,6-*d*]oxazole **8b**. No traces of the corresponding oxazin-2-ones were detected.

Scheme 2

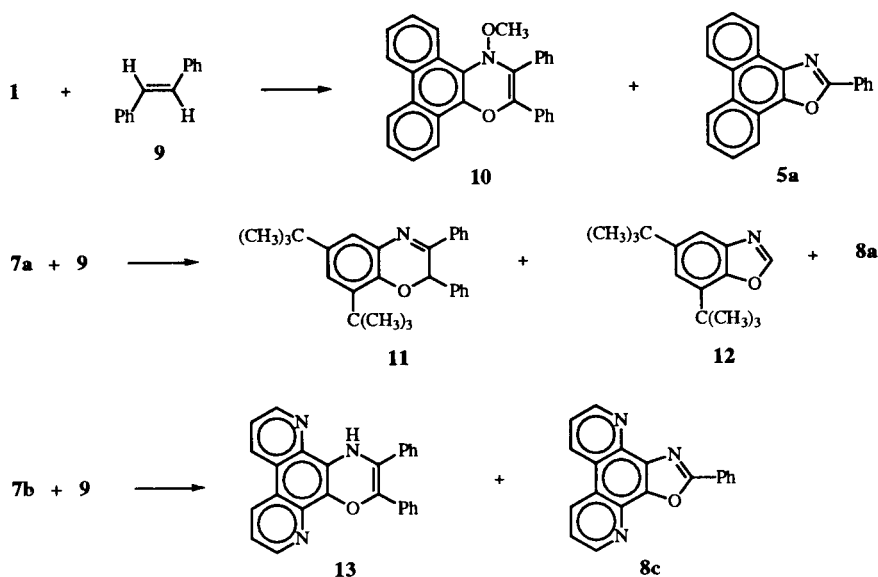


- 7a, R₁ = R₃ = H, R₂ = R₄ = C(CH₃)₃
 b, R₁-R₂ = R₄-R₃ = -N=CH-CH=CH
 8a, R₁ = R₃ = H, R₂ = R₄ = C(CH₃)₃, R₅ = H
 b, R₁-R₂ = R₄-R₃ = -N=CH-CH=CH-, R₅ = OCH₃

The forementioned monoximes were subsequently brought into reaction with *trans*-stilbene, aiming at the synthesis of the corresponding 2*H*-1,4-benzoxazines. We already reported [1] that refluxing a dioxane solution of the oxime **1** and dimethyl acetylenedicarboxylate (DMAD) leads to dimethyl 7-oxo-7*H*-dibenzo[*de,g*]quinoline-4,5-dicarboxylate (25%) via a [4+2] cycloaddition of the dienophile across the heterodiene system -C=C-C=N-OCH₃, extending from the exocyclic imino bond to the aromatic ring system, and further methanol elimination. In contrast, treatment of 1-nitroso-2-naphthol (bearing as well the tautomeric form of *o*-benzoquinone monoxime), or phenanthrenequinone monoxime with 1,1-bis[*p*-(dimethylamino)phenyl]ethylenes in presence of a catalytic amount of glacial acetic acid affords [7] 2*H*-1,4-oxazines in good yields, while action of 2-methylene-1,3,3-trimethyl-2,3-dihydroindole on 1,8-bishydroxyiminoanthracene-2,7-dione results [8] in the analogous dispiroanthra-bisoxazine derivatives. In both cases, the [4+2] addition product formed is further dehydrated. In a similar manner, cycloaddition reactions of some *o*-quinone monoximes with electron rich alkenes lead [9] to the corresponding 4-aryl-2,3-dihydro-4*H*-1,4-benzoxazine derivatives.

A mixture of equimolecular amounts of the monoxime **1** and *trans*-stilbene **9** is heated at 140° for 105 minutes and the reaction mixture is then separated by column chromatography to yield 13% of the Diels Alder addition product 4-methoxy-2,3-diphenylphenanthro[9,10-*b*][1,4]oxazine **10**, 45% of the above mentioned oxazole **5a** and 10% of phenanthrene-9,10-quinone. Furthermore, by heating an equimolar mixture of the monoxime **7a** and the dienophile **9** under similar conditions for 22 hours, compounds **11** (5%), **8a** (20%) and **12** (12%) were obtained. Prolonged heating (10 days) of **7b** with 2.5 equivalents of **9** leads to 10% of the oxazine **13** and 3% of the oxazole **8c**. It should be noticed that **11** was partially transformed to **8a** upon recrystallization from boiling ethanol, an observation confirmed by control experiment. Indeed, the oxazine in question totally overwent to the corresponding oxazole when heated at 140° for 18 hours. The structures proposed for compounds **10**, **11**, **13** are in full agreement with their spectroscopic and analytical data, especially concerning the lack of saturated ring carbon atoms in **10**, as well as the presence of the -OCH₃ group in the same oxazine, of the methinic -CH in **11** (¹H nmr δ 6.31 ppm) and of the -NH group in **13** (ir 3370 cm⁻¹). Obviously, further evidence is necessary in order to elucidate the products of the above detailed interactions. At a first approach the different character of the disubstituted benzene ring compared to that of the fused ones should be pointed out.

Scheme 3



EXPERIMENTAL

Melting points are uncorrected and were determined on a Kofler hot stage apparatus. The ir spectra were determined with a Perkin Elmer 297 spectrophotometer as nujol mulls. The ^1H and ^{13}C nmr spectra were recorded with deuteriochloroform as solvent on a Bruker Model AM 300 (300 MHz) spectrometer with TMS as the internal standard. Mass spectra were determined on a 250 VG spectrometer. The ionization energy was maintained at 70 eV. Light petroleum refers to the 40-60° fraction.

Reaction of 10-(Methoxyimino)phenanthren-9-one **1** with Methyl Phenylacetate **2a**.

A solution of 10-(methoxyimino)phenanthren-9-one **1** (0.410 g, 1.68 mmoles) in an excess amount of methyl phenylacetate **2a** (2 ml) was heated at 190° for 35 minutes. Part of 3-phenyl-2*H*-phenanthro[9,10-*b*][1,4]oxazin-2-one **4a** crystallized on cooling, the rest being obtained by column chromatographic separation of the residue on silica gel (eluant light petroleum/ethyl acetate 3:1), 0.140 g (25%), mp 233-235° (light petroleum/ethyl acetate); ir (nujol): 1725, 1610, 1592, 1280 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 7.39-7.81 (m, 7H), 8.37-8.79 (m, 5H), 8.80-9.00 (m, 1H); ms: m/z (%) 323 (M^+ , 79), 295 (100), 164 (92), 105 (10).

Anal. Calcd. for $\text{C}_{22}\text{H}_{13}\text{NO}_2$: C, 81.72; H, 4.05; N, 4.33. Found: C, 82.01; H, 4.32; N, 4.33.

The fraction eluted next gave 2-phenylphenanthro[9,10-*d*]oxazole **5a**, 0.053 g, (10%), mp 204-205° (dichloromethane/methanol) (lit [11] 205-206°).

Reaction of 10-(Methoxyimino)phenanthren-9-one **1** with Ethyl 4-Methylphenylacetate **2b**.

A solution of 10-(methoxyimino)phenanthren-9-one **1** (0.410 g, 1.68 mmoles) in an excess amount of ethyl 4-methylphenylacetate **2b** (1 ml) was heated at 190° for 40 minutes. Part of 3-(4-methylphenyl)-2*H*-phenanthro[9,10-*b*][1,4]oxazin-2-one **4b** crystallized on cooling, the rest being obtained

by column chromatographic separation of the residue on silica gel (eluant dichloromethane), 0.124 g (25%), mp 240-242° (benzene); ir (nujol): 1729, 1645, 1619, 1589, 1280, 1258, 1172 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 2.47 (s, 3H), 7.33-7.83 (m, 6H), 7.96-8.08 (m, 2H), 8.46-8.66 (m, 3H), 8.89-8.95 (m, 1H); ms: m/z (%) 337 (M^+ , 29), 309 (100), 206 (21), 164 (35), 119 (88).

Anal. Calcd. for $\text{C}_{23}\text{H}_{15}\text{NO}_2$: C, 81.88; H, 4.48; N, 4.15. Found: C, 82.02; H, 4.48; N, 4.18.

The fraction eluted next gave 2-(4-methylphenyl)phenanthro[9,10-*d*]oxazole **5b**, 0.050 g (10%), mp 244-246° (dichloromethane) (lit [12] 246-248°).

Reaction of 10-(Methoxyimino)phenanthren-9-one **1** with Ethyl 4-Nitrophenylacetate **2c**.

A mixture of 10-(methoxyimino)phenanthren-9-one **1** (0.237 g, 1 mmole) and the equimolar amount of ethyl 4-nitrophenylacetate (0.209 g, 1 mmole) **2c** was heated at 190° for 35 minutes. Column chromatographic separation of the residue on silica gel (eluant dichloromethane) yielded 3-(4-nitrophenyl)-2*H*-phenanthro[9,10-*b*][1,4]oxazin-2-one **4c**, 0.124 g (25%), mp 240-242° (benzene); ir (nujol): 1722, 1605, 1595, 1309, 1246, 1173 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 7.59-7.95 (m, 4H), 7.99-9.12 (m, 8H); ms: m/z (%) 368 (M^+ , 52), 340 (100), 310 (28), 294 (58), 164 (44), 163 (55).

Anal. Calcd. for $\text{C}_{22}\text{H}_{12}\text{N}_2\text{O}_4$: C, 71.73; H, 3.28; N, 7.60. Found: C, 71.80; H, 3.33; N, 7.63.

The fraction eluted next gave 2-(4-nitrophenyl)phenanthro[9,10-*d*]oxazole **5c**, 0.050 g (11%), mp 244-246° (dichloromethane) (lit [14] 246-248°).

Reaction of 10-(Methoxyimino)phenanthren-9-one **1** with Methyl 4-Methoxyphenylacetate **2d**.

A solution of 10-(methoxyimino)phenanthren-9-one **1** (0.410 g, 1.68 mmoles) in an excess amount of methyl 4-methoxyphenylacetate **2d** (0.5 ml) was heated at 190° for 40 minutes. Part of 3-(4-methoxyphenyl)-2*H*-phenanthro[9,10-*b*][1,4]oxazin-2-one **4d** crystallized on cooling, the rest being obtained by column chromatographic separation of the residue

on silica gel (eluant dichloromethane), 0.126 g (28%), mp 227-229° (light petroleum/dichloromethane); ir (nujol): 1729, 1599, 1307, 1246, 1173 cm⁻¹; ¹H nmr (deuteriochloroform): δ 3.39 (s, 3H), 7.05-7.10 (m, 3H), 7.71-7.83 (m, 4H), 8.54-8.59 (m, 1H), 8.61-8.72 (m, 3H), 8.98-9.01 (m, 1H); ms: m/z (%) 353 (M⁺, 48), 325 (100), 310 (26), 282 (13), 164 (20), 163 (30).

Anal. Calcd. for C₂₃H₁₅NO₃: C, 78.19; H, 4.27; N, 3.96. Found: C, 78.30; H, 4.41; N, 3.95.

The fraction eluted next gave 2-(4-methoxyphenyl)phenanthro[9,10-*d*]oxazole **5d**, 0.020 g (5%), mp 222-224° (light petroleum/dichloromethane) (lit [13] 222-223°).

Reaction of 10-(Methoxyimino)phenanthren-9-one **1** with Ethyl 2-Naphthylacetate **2e**.

A solution of 10-(methoxyimino)phenanthrene-9-one **1** (0.410 g, 1.68 mmoles) in an excess amount of ethyl 2-naphthylacetate **2e** (0.5 ml) was heated at 190° for 105 minutes. Column chromatographic separation of the residue on silica gel (eluant light petroleum/ethyl acetate) yielded 2-(2-naphthyl)phenanthro[9,10-*d*]oxazole **5e**, 0.060 g (17%), mp 252-254° (light petroleum/dichloromethane) (lit [12] 252-255°).

Reaction of 10-(Methoxyimino)phenanthren-9-one **1** with Ethyl 3-Pyridylacetate **2f**.

A mixture of 10-(methoxyimino)phenanthrene-9-one **1** (0.410 g, 1.68 mmoles) and an excess amount of ethyl 3-pyridylacetate **2f** (0.3 ml) was heated at 190° for 10 minutes. Column chromatographic separation of the residue on silica gel (eluant light petroleum/dichloromethane/ethyl acetate 1:3:0 to 0:10:1) yielded 3-(3-pyridyl)-2*H*-phenanthro[9,10-*b*][1,4]oxazin-2-one **4f**, 0.118 g (29%), mp 248-250° (dichloromethane/ethanol); ir (nujol): 1724, 1609, 1586, 1295, 1281, 1121 cm⁻¹; ¹H nmr (deuteriochloroform): δ 7.39-8.22 (m, 7H), 8.31-8.43 (m, 1H), 8.55-8.80 (m, 3H), 8.93-9.03 (m, 1H); ms: m/z (%) 324 (M⁺, 42), 296 (100), 190 (7), 164 (52), 163 (45).

Anal. Calcd. for C₂₀H₁₂N₂O₂: C, 76.91; H, 3.87; N, 8.97. Found: C, 77.08; H, 3.78; N, 8.80.

Reaction of 10-(methoxyimino)phenanthren-9-one **1** with 4-Methoxyphenylacetic Acid **2g**.

A mixture of 10-(methoxyimino)phenanthrene-9-one **1** (0.237 g, 1 mmole) and the equimolar amount of 4-methoxyphenylacetic acid **2g** was heated at 190° for 60 minutes. Column chromatographic separation of the residue on silica gel (eluant light petroleum/dichloromethane) yielded 3-(4-methoxyphenyl)-2*H*-phenanthro[9,10-*b*][1,4]oxazin-2-one **4d**, 0.020 g (6%), mp 227-229° (light petroleum/dichloromethane). The spectroscopic and analytical data fully agree with those given above.

The fraction eluted next gave 2-(4-methoxyphenyl)phenanthro[9,10-*d*]oxazole **5d**, 0.049 g (15%), mp 226-227° (light petroleum/dichloromethane) (lit [13] 222-223°).

Reaction of 10-(Methoxyimino)phenanthren-9-one **1** with 2-Naphthylacetic Acid **2h**.

A mixture of 10-(methoxyimino)phenanthrene-9-one **1** (0.237 g, 1 mmole) and the equimolar amount of 2-naphthylacetic acid **2h** (0.186 g, 1 mmole) was heated at 190° for 15 minutes. At crystallization the residue yielded 2-(2-naphthyl)phenanthro[9,10-*d*]oxazole **5e**, 0.603 g (22%), mp 252-254° (light petroleum/dichloromethane) (lit [12] 252-255°).

Reaction of 10-(Methoxyimino)phenanthren-9-one **1** with 3-Pyridylacetic Acid **2i**.

A mixture of 10-(methoxyimino)phenanthrene-9-one **1** (0.237 g, 1 mmole) and the equimolar amount of 3-pyridylacetic acid **2i** (0.172 g, 1 mmole) was heated at 190° for 10 minutes. Column chromatographic separation of the residue on silica gel (eluant light petroleum/ethyl acetate 5:1 to 1:2) yielded phenanthro[9,10-*d*]oxazole **6**, 0.379 g (18%), mp 148-150° (ethanol) (lit [1] 148-149°).

The fraction eluted next gave 3-(3-pyridyl)-2*H*-phenanthro[9,10-*b*][1,4]oxazin-2-one **4f**, 0.004 g (1.5%), mp 248-250° (dichloromethane/ethanol). The spectroscopic and analytical data fully agree with those given above.

Reaction of 10-(Methoxyimino)phenanthren-9-one **1** with 4-Hydroxyphenylacetic Acid **2j**.

A mixture of 10-(methoxyimino)phenanthren-9-one **1** (0.237 g, 1 mmole) and the equimolar amount of 4-hydroxyphenylacetic acid **2j** (0.152 g, 1 mmole) was heated at 190° for 25 minutes. Column chromatographic separation of the residue on silica gel (eluant light petroleum/ethyl acetate 2:1 to 10:7) yielded 2-(4-hydroxyphenyl)phenanthro[9,10-*d*]oxazole **5g**, 0.058 g (19%), mp >310° (ethyl acetate); ir (nujol): 3400, 1600, 1369, 1280 cm⁻¹; ¹H nmr (deuteriochloroform): δ 6.86-7.24 (m, 2H), 7.49-8.98 (m, 10H); ms: m/z (%) 311 (M⁺, 100), 164 (8), 163 (22).

Anal. Calcd. for C₂₁H₁₃NO₂: C, 81.01; H, 4.20; N, 4.49. Found: C, 80.90; H, 4.28; N, 4.59.

Reaction of 2-Methoxyimino-4,6-di-*t*-butylbenzen-1-one **7a** with Ethyl Phenylacetate **2a**.

A solution of 2-methoxyimino-4,6-di-*t*-butylbenzen-1-one **7a** (0.249 g, 1 mmole) in an excess amount of ethyl phenylacetate **2a** (1 ml) was heated at 190° for 330 minutes. Column chromatographic separation of the residue on silica gel (eluant dichloromethane/ethyl acetate 10:1) yielded 2-phenyl-5,7-di-*t*-butylbenzoxazole **8a**, 0.041 g (17%), mp 81-82° (lit [15] mp 82-84°); ir (nujol): 1595, 1550, 1278 cm⁻¹; 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⁺, 69), 292 (100), 237 (24), 198 (5), 105 (11).

Reaction of 6-(Methoxyimino)[4,7]phenanthrolin-5-one **7b** with Methyl 4-Methoxyphenylacetate **2d**.

A solution of 6-(methoxyimino)[4,7]phenanthrolin-5-one **7b** (0.239 g, 1 mmole) in an excess amount of methyl 4-methoxyphenylacetate **2d** (1 ml) was heated at 190° for 60 minutes. Column chromatographic separation of the residue on silica gel (eluant light petroleum/ethyl acetate/methanol 1:1:0 to 0:0:1) yielded 2-(4-methoxyphenyl)[4,7]phenanthrolin[5,6-*d*]oxazole **8b**, 0.141 g (43%), mp 292-294° (dichloromethane/ethyl acetate); ir (nujol): 1600, 1579, 1509, 1252, 1159 cm⁻¹; ¹H nmr (deuteriochloroform): δ 3.92 (s, 3H), 7.08 (d, J = 9 Hz, 2H), 7.65-7.73 (m, 2H), 8.53 (d, J = 9 Hz, 2H), 8.96-9.14 (m, 2H), 9.15-9.21 (m, 2H); ms: m/z (%) 327 (M⁺, 97), 312 (20), 284 (19), 256 (11), 165 (9), 139 (4).

Anal. Calcd. for C₂₀H₁₃N₃O₂: C, 73.38; H, 4.00; N, 12.22. Found: C, 73.45; H, 4.10; N, 12.19.

Reaction of 10-(Methoxyimino)phenanthren-9-one **1** with *trans*-stilbene **9**.

A mixture of 10-(methoxyimino)phenanthren-9-one **1** (0.300 g, 1.26 mmoles) and **9** (0.277 g, 1.26 mmoles) was heated at 140° for 105 minutes. Column chromatographic separation of

the residue on silica gel (eluant light petroleum/dichloromethane 1:3 to 1:10) yielded 4-methoxy-2,3-diphenylphenanthro[9,10-*b*]-[1,4]oxazine **10**, 0.068 g (13%), mp 158-160° (dichloromethane/ethanol); ir (nujol): 1601, 1175 cm⁻¹; ¹H nmr (deuteriochloroform): δ 3.47 (s, 3H), 7.28-7.37 (m, 8H), 7.56-7.76 (m, 6H), 8.33 (d, J = 6 Hz, 1H), 8.64 (d, J = 9 Hz, 2H), 8.95 (d, J = 6 Hz, 1H); ¹³C nmr (deuteriochloroform): δ 154.0, 140.7, 137.9, 136.1, 131.2, 130.2, 129.9, 129.0, 128.8, 128.3, 128.0, 127.6, 127.3, 126.8, 126.7, 126.4, 125.1, 124.1, 122.8, 122.7, 122.4, 120.5, 99.9, 52.1; ms: m/z (%) 415 (M⁺, 17), 400 (6), 295 (9), 164 (8), 105 (100).

Anal. Calcd. for C₂₉H₂₁N₃O₂: C, 83.83; H, 5.09; N, 3.37. Found: C, 83.89; H, 5.14; N, 3.50.

The fraction eluted next gave 2-phenyl-phenanthro[9,10-*d*]oxazole **5a**, 0.169 g, 45%, mp 204-205° (dichloromethane/ethanol) (lit [11] 205-206°).

Reaction of 2-(Methoxyimino)-4,6-di-*t*-butylbenzen-1-one **7a** with *trans*-stilbene **9**.

A mixture of 2-(methoxyimino)-4,6-di-*t*-butylbenzen-1-one **7a** (0.249 g, 1 mmole) and **9** (0.180 g, 1 mmole) was heated at 140° for 22 hours. Column chromatographic separation of the residue on silica gel (eluant light petroleum/dichloromethane 1:3 to 0:1) yielded 6,8-di-*t*-butyl-2,3-diphenyl-2*H*-benz[1,4]oxazine **11**, 0.018 g (5%), mp 125-126° (methanol); ir (nujol): 1590, 1558, 1173 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.21 (s, 9H), 1.29 (s, 9H), 6.31 (s, 1H), 6.99-7.52 (m, 10H), 7.71-8.05 (m, 2H); ms: m/z (%) 397 (M⁺, 100), 383 (14), 178 (35), 167 (14).

Anal. Calcd. for C₂₈H₃₁NO: C, 84.59; H, 7.86; N, 3.52. Found: C, 84.68; H, 7.79; N, 3.53.

The fraction eluted next gave 2-phenyl-5,7-di-*t*-butylbenzoxazole **8a**, 0.060 g (20%), mp 81-82°. The spectroscopic and analytical data fully agree with those given above.

The fraction eluted next gave 5,7-di-*t*-butylbenzoxazole **12**, 0.028 g (12%), oil (lit [16] mp not given); ir (nujol): 1607, 1515, 1238 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.36 (s, 9H), 1.47 (s, 9H), 8.04 (s, 1H), 7.66 (s, 1H), 7.33 (s, 1H); ms: m/z (%) 231 (M⁺, 29), 217 (100), 201 (30), 189 (21), 115 (20).

Reaction of 6-Methoxyimino[4,7]phenanthrolin-5-one **7b** with *trans*-stilbene **9**.

A mixture of 6-methoxyimino[4,7]phenanthrolin-5-one **7b** (0.239 g, 1 mmole) and **9** (0.440 g, 2.44 mmoles) was heated at 140° for 10 days. Column chromatographic separation of the residue on silica gel (eluant ethyl acetate/methanol 1:0 to 0:1) yielded 2,3-diphenyl-1*H*-[4,7]phenanthroliino[5,6-*b*][1,4]oxazine **13**, 0.035 g (10%), mp >300° (chloroform/ethyl acetate); ir (nujol): 3370, 1581, 1543 cm⁻¹; ¹H nmr (deuteriochloroform): δ

7.41-7.80 (m, 8H), 8.40-8.73 (m, 2H), 8.80-9.20 (m, 6H); ¹³C nmr (deuteriochloroform): δ 164.3, 151.2, 151.0, 150.7, 146.8, 141.9, 139.5, 137.4, 131.6, 131.5, 131.3, 128.8, 128.5, 128.0, 127.6, 126.8, 123.8, 123.5, 121.5; ms: m/z (%) 297 (M⁺-90 [PhCH], 100), 268 (6), 192 (11), 166 (40), 139 (18).

Anal. Calcd. for C₂₆H₁₇N₃O: C, 80.59; H, 4.42; N, 10.84. Found: C, 80.85; H, 4.40; N, 10.90.

The fraction eluted next gave 2-(4-methoxyphenyl)[4,7]-phenanthroliino[5,6-*d*]oxazole **8c**, 0.010 g (3%), mp 292-294° (chloroform/ethyl acetate); ir (nujol): 1600, 1579, 1509, 1272 cm⁻¹; ¹H nmr (deuteriochloroform): δ 3.92 (s, 3H), 7.08 (d, J = 9 Hz, 2H), 7.65-7.73 (m, 2H), 8.53 (d, J = 9 Hz, 2H), 8.96-9.14 (m, 2H), 9.15-9.21 (m, 2H); ms: m/z (%) 327 (M⁺, 97), 312 (20), 284 (19), 256 (11), 165 (9), 139 (4).

Anal. Calcd. for C₂₀H₁₃N₃O₂: C, 73.38; H, 4.00; N, 12.22. Found: C, 73.45; H, 4.10; N, 12.19.

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