An Unusual Route for the Regioselective Acylation of Polycyclic Aromatic Hydrocarbons: Nitrile Oxide Addition Followed by Isoxazoline Degradation

Antonino Corsaro, Ugo Chiacchio, Vito Librando, Venerando Pistarà,* Antonio Rescifina

Dipartimento di Scienze Chimiche, Università di Catania, viale A. Doria 6, I-95125 Catania, Italy

Fax +39(95)580138; E-mail: acorsaro@dipchi.unict.it

Received 18 February 2000; revised 19 May 2000

Abstract: By treatment with a base such as sodium methoxide or surprisingly lithium aluminium hydride monocycloadducts **1a–c** afforded the corresponding oximes **2a–c** which were oxidized to ketones **3a–c** by the Dess–Martin method. The same ketones **3a–c** are obtained by reductive ring opening of **1a–c** with Raney-Ni. Monocycloadducts **1d–h** also gave oximes **2d–h** upon treatment with the same bases, but complex reaction mixtures were obtained when oximes **2d–h** were subjected to oxidation or monocycloadducts **1d–h** were subjected to reduction with Raney-Ni.

Key words: polycyclic aromatic hydrocarbons, hydrogenations, ketones, oximes, oxidations, ring opening

In the last two decades, 1,3-dipolar cycloadditions of nitrile oxides with aromatics[1] and heteroaromatics[1,2] have received a great deal of interest since these aromatics show an unexpected dipolarophilic reactivity against any possible chemical inactivity due to the high loss of aromaticity involved in their cycloaddition processes.

Recently we investigated the behavior of some polycyclic aromatic hydrocarbons[3] (PAHs) and their aza-analogs[4] (*N*-PAHs) towards nitrile oxides and found that pyrene, anthracene, phenanthrene and perylene add mesitonitrile oxide and its dichloro derivative to afford modest yields of mono- and bis-cycloadducts. In the case of anthracene the cycloaddition was site- and regioselective. By using the technique of microwave irradiation the above cycloadditions afforded improved yields of products and in particular their reaction times were dramatically shortened.[5] Some aza-analogs of phenanthrene, phenanthridine, 1,10-, 4,7- and 1,7-phenanthroline, add to mesitonitrile oxide to give low yields of the corresponding monocycloadducts; 4,7-phenanthroline also gives some other minor products among which the bis-cycloadduct to a pyridine ring was isolated. Phenanthridinone is obtained in the case of phenanthridine from the non-isolable monocycloadduct.[4]

The construction of the dihydroisoxazole ring on the C=C double bond of PAHs offers an interesting possibility of introducing one or two functions on a ring of these PAHs through the well known cleavage of the dihydroisoxazole N–O or C–O bond which have been extensively investigated in the past years and leads to the conversion of the dihydroisoxazole ring into α,β-unsaturated oximes or ketones, β-hydroxy ketones and γ-amino alcohols.[6]

By applying this synthetic methodology, which in our hands has included the treatment with acidic, basic and reducing agents, of previously reported monocycloadducts **1a–c**,**e–h** of mesitonitrile oxide to the above PAHs[3,5] and *N*-PAHs,[4] and to monocycloadduct **1d** of acridine,[7] we found that, among the other results, ketones **3a–c** can be prepared by base-induced cleavage of the C–O bond or by hydrogenolytic cleavage of the N–O bond of the dihydroisoxazole ring (Scheme 1).

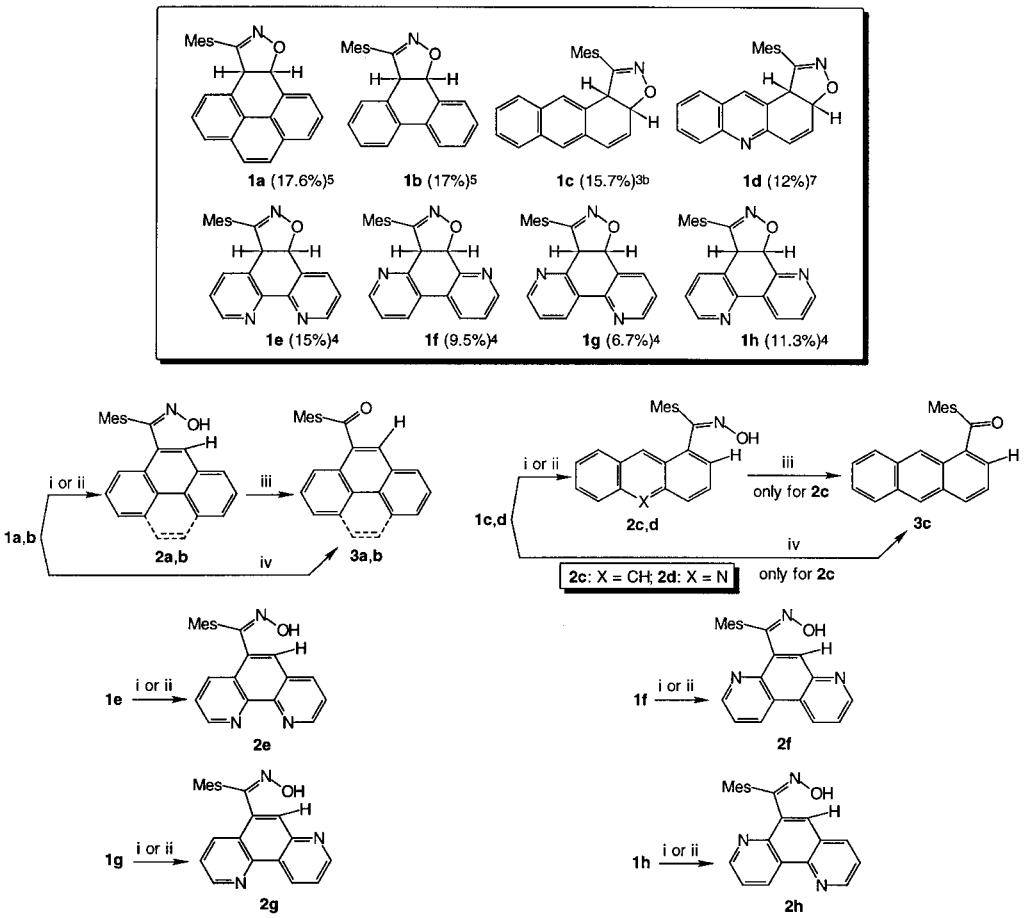
Monocycloadducts **1a–c** are stable upon exposure to concentrated hydrochloric acid and 50% sulfuric acid at room temperature and to heat up to 100 °C, while they undergo the scission of O-C_5 bond of the dihydroisoxazole ring when treated with bases such as sodium methoxide to give the corresponding oximes **2a–c** in very good yields (Scheme 1, Table).

The conversion of oximes **2a–c** into the corresponding ketones **3a–c** cannot be accomplished by simple acidic or basic hydrolysis, but only by oxidation methods among which the Dess–Martin's periodinane (DMP) procedure[8] gave fair yields of ketones **3a–c** (Scheme 1, Table).

Monocycloadducts **1a–c** were subjected to catalytic hydrogenation with Raney-Ni or Pd-C and chemical reduction with lithium aluminium hydride, which latter has surprisingly produced oximes **2a–c** in good yields (Table), thus acting as a base rather than a reducing agent, probably because of the aromatization of the PAH ring. The catalytic hydrogenation of **1a–c** with Raney-Ni under hydrogen atmosphere (30 psi) in methanol containing aqueous boric acid, afforded good yields of the same ketones **3a–c** (Table), obtained by oxidation of oximes **2a–c** with DMP (Scheme 1).

These ketones represent the final products of the reaction sequence which involves the initial hydrogenolytic cleavage of the N–O bond to the transient imino alcohols **4a–c** and successively the dehydration and hydrolysis of the imine group to give again aromatic PAHs (Scheme 2). This synthetic strategy for aromatic ketones of PAHs appears very interesting because it allows one to obtain, unlike traditional methods of aroylation of PAHs,[9] an unique ketone, which is the 1-substituted and not the 9-substituted[10] derivative in the case of anthracene.

The catalytic hydrogenation with Pd-C in methanol (H_2, 60 psi, 10 h) led to the isolation of the ketone **3b** (82%) in the case of **1b**, while **1a** and **1c** gave **6** (65%) and **7** (60%) (Figure), respectively (see Experimental). Ketone **6** is derived cleanly from ketone **3a** by further reduction of phenyl rings having bonds with characteristic features of double bonds, while **7** is derived from **1b** by reduction of



Reagents and conditions: i) NaOMe/MeOH, reflux; ii) $LiALH_4$,/THF, 0 °C; iii) DMP/CH_2Cl_2, r.t.; iv) Raney-Ni/H_2 (30 psi)/MeOH/H_3BO_3/H_2O, 8 h, r.t.

Scheme 1

the only two external phenyl rings, which maintains the unchanged dihydroisoxazole ring.

Also mocycloadducts of *N*-PAHs **1d–h** are stable to acidic reagents and they undergo the dihydroisoxazole ring opening by treatment with sodium methoxide or lithium aluminium hydride to give the corresponding oximes **2d–h**. These were resistant to acidic and basic hydrolysis and gave complex reaction mixtures by oxidative methods. When **1d–h** were subjected to reduction with Raney-Ni or Pd-C, complex reaction mixtures were obtained, the ^1H and ^{13}C NMR spectra of which indicated the presence of many products derived from the opening of the dihydroisoxazole ring and reduction of *N*-PAH nucleus. All these crude materials were not further separated because they were not considered synthetically useful.

Table Yields of Oximes **2a**–**h** and Ketones **3a**–**c**

Reaction Conditions	Product										
	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**3a**	**3b**	**3c**
MeO^-Na^+/MeOH	96	97	91	86	92	81	87	86	-	-	-
$LiAlH_4$/THF	83	88	77	73	74	75	77	70	-	-	-
DMP/CH_2Cl_2	-	-	-	-	-	-	-	-	60	62	54
Raney-Ni/MeOH	-	-	-	-	-	-	-	-	80	84	78

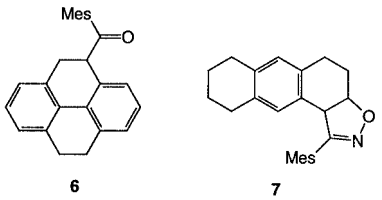
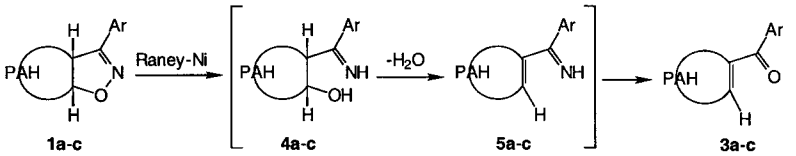


Figure Structures of compounds **6** and **7**

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. IR spectra were taken on a Perkin-Elmer Paragon 500 FT-IR Spectrometer using KBr discs, NMR spectra were recorded on a Varian instrument at 200 or 500 MHz (^1H) and at 50 or 125 MHz (^{13}C) using TMS as internal standard and $CDCl_3$ as solvent. Elemental analyses were performed on a Carlo Erba Elemental Analyser 1106. TLC separations were performed on Merck silica gel 60-F_{254} precoated aluminium plates. Preparative chromatographic separations were conducted by means of flash chromatog-



Scheme 2

raphy using Merck silica gel 60 (0.035–0.070 mm) with cyclohexane/EtOAc mixtures as eluents. Monocycloadducts **1a–c**,**e–h** were obtained according to the previously reported cycloaddition reactions[3–5] of mesitonitrile oxide with PAHs and *N*-PAHs. Physical and spectral data of monocycloadduct **1d**[7] will be reported elsewhere.

Conversion of 1a–h into Oximes 2a–h; General Procedure

Method A: To a solution of dihydroisoxazoles **1a–h** (2 mmol) in anhyd MeOH (20 mL) was added a solution of 0.1 M MeONa in MeOH (20 mL) and the resulting mixture was refluxed until the starting material disappeared (ca. 30 min). After removal of the solvent under reduced pressure, the residue was taken again with H_2O (30 mL), extracted with EtOAc (3 × 20 mL), dried (Na_2SO_4) and concentrated under reduced pressure to give oximes **2a–h**, which were purified by chromatography and crystallized from EtOAc.

Method B: To a stirred solution of dihydroisoxazoles **1a–h** (2 mmol) in anhyd THF (20 mL) was added $LiAlH_4$ (60 mmol) at 0 °C and the mixture was allowed to react under stirring until the starting material had disappeared (4 h). After hydrolysis, the mixture was diluted with CH_2Cl_2 and then the organic layer was washed with H_2O (20 mL), dried (Na_2SO_4) and concentrated under reduced pressure to give oximes **2a–h**, which were purified by chromatography and crystallized from EtOAc.

Conversion of Oximes 2a–c into Ketones 3a–c; General Procedure

To a stirred solution of oximes **2a–c** (1 mmol) in CH_2Cl_2 (20 mL) saturated with H_2O prior to use, DMP (1.1 mmol) was add at r.t. The mixture was allowed to react under vigorous stirring until oximes **2a–c** were consumed and then it was diluted with 5% aq Na_2SO_4 solution (10 mL) followed by H_2O (10 mL). The organic layer was washed with H_2O (20 mL), dried (Na_2SO_4) and then concentrated under reduced pressure to give ketones **3a–c** which were purified by chromatography and crystallized from EtOAc.

Conversion of 1a–c into Ketones 3a–c; General Procedure

In a hydrogenation vessel a suspension of **1a–c** (2 mmol), a spatula tip (estimated ca. 400 mg) of Raney-Nickel, MeOH (15 mL), H_2O (3 mL) and H_3BO_3 (5 mmol) were placed. The vessel was mechanically shaken for 3 h under a hydrogen atmosphere (30 psi). The mixture was then filtered through Celite® into a separatory funnel containing a 10% aq $NaHCO_3$ solution (10 mL) and CH_2Cl_2 (20 mL). After separation, the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL) and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure to yield crude ketones **3a–c** which were crystallized from EtOAc. Alternatively, cycloadducts **1a–c** (2 mmol) and a spatula tip of Pd/C (10%) were used under an hydrogen atmosphere (60 psi) for 10 h, but only **1b** gave the corresponding ketone **3b**; surprisingly, cycloadducts **1a** and **1c** gave compounds **6** and **7**, respectively.

Mesityl(pyren-4-yl)methanone Oxime (2a)

Yield: 96% by treatment with MeONa; 83% by treatment with $LiAlH_4$; white crystals; mp 164–166 °C.

IR (KBr): ν = 3280, 1607 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 2.28 (s, 6 H, CH_3), 2.39 (s, 3 H, CH_3), 7.03 (s, 2 H, Mes H), 7.75 (s, 1 H, pyrene H), 7.93–8.27 (m, 7 H, pyrene H), 9.50 (dd, 1 H, *J* = 1.2, 8.0 Hz, pyrene H), 9.56 (br s, 1 H, OH).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 19.93 and 21.25 (CH_3), 124.55, 125.05, 125.72, 125.78, 125.93, 126.26, 126.76, 128.05, 128.45, 128.57, 130.03, 130.13, 130.96, 131.37, 131.46, 135.79, 138.50 (aromatic C), 157.15 (oxime C).

Anal. calcd for $C_{26}H_{21}NO$ (363.4) C, 85.92; H, 5.82; N, 3.85. Found: C, 86.01; H, 8.85; N, 3.91.

MS: *m*/*z* = 363 (M^+), 362 (M – 1)$^+$, 346 (M – 17)$^+$, 201 (M – 162)$^+$.

Mesityl(9-phenanthryl)methanone Oxime (2b)

Yield: 97% by treatment with MeONa; 88% by treatment with $LiAlH_4$; white crystals; mp 185–187 °C.

IR (KBr): ν = 3276, 1609 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.24 (s, 3 H, CH_3), 2.27 (s, 6 H, CH_3), 6.85 (s, 2 H, Mes H), 7.41 (s, 1 H, phenanthrene H), 7.50 (t, 1 H, *J* = 7.5 Hz, phenanthrene H), 7.61 (t, 1 H, *J* = 7.5 Hz, phenanthrene H), 7.67 (m, 2 H, phenanthrene H), 7.71 (d, 1 H, *J* = 7.5 Hz, phenanthrene H), 8.13 (m, 1 H, phenanthrene H), 8.64 (d, 1 H, *J* = 8.5 Hz, phenanthrene H), 8.71 (m, 1 H, phenanthrene H), 9.41 (br s, 1 H, OH).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.82 and 20.99 (CH_3), 122.54, 122.81, 126.16, 126.57, 127.51, 127.88, 128.38, 128.97, 129.11, 129.17, 130.03, 130.80, 130.95, 131.65, 133.98, 137.73, 138.28 (aromatic C), 156.00 (oxime C).

Anal. calcd for $C_{24}H_{21}NO$ (339.4) C, 84.92; H, 6.24; N, 4.13. Found: C, 84.04; H, 6.35; N, 4.28.

MS: *m*/*z* = 339 (M^+), 338 (M – 1)$^+$, 322 (M – 17)$^+$, 177 (M – 162)$^+$.

Mesityl(1-anthryl)methanone Oxime (2c)

Yield: 91% by treatment with MeONa; 77% by treatment with $LiAlH_4$; white crystals; mp 153–155 °C.

IR (KBr): ν = 3280, 1609 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 2.25 (s, 6 H, CH_3), 2.28 (s, 3 H, CH_3), 6.88 (s, 2 H, Mes H), 7.69–7.79 (m, 5 H, anthracene H), 8.09 (m, 1 H, anthracene H), 8.24 (m, 1 H, anthracene H), 8.40 (m, 1 H, anthracene H), 9.20 (br s, 1 H, OH).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 20.85 and 21.0 (CH_3), 126.73, 127.26, 128.63, 129.23, 132.46, 132.78, 133.16, 133.60, 134.27, 134.94, 135.11, 135.84, 135.90, 136.89, 138.85 (aromatic C), 157.09 (oxime C).

Anal. calcd for $C_{24}H_{21}NO$ (339.4): C, 84.92; H, 6.24; N, 4.13. Found C, 85.08; H, 6.31; N, 4.22.

MS: *m*/*z* = 339 (M^+), 338 (M – 1)$^+$, 322 (M – 17)$^+$, 117 (M – 162)$^+$.

Mesityl(acridin-1-yl)methanone Oxime (2d)

Yield: 86% by treatment with MeONa; 73% by treatment with $LiAlH_4$; white crystals; mp 160–162 °C.

IR (KBr): ν = 3276, 1610 cm^{-1}.

^1H NMR ($CDCl_3$ 200 MHz): δ = 2.18 (s, 6 H, CH_3), 2.37 (s, 3 H, CH_3), 7.01 (m, 2 H, Mes H), 7.18 (dd, 1 H, *J* = 7.2, 1 Hz, acridine

H), 7.59 (m, 3 H, acridine H), 7.82 (dd, 1 H, *J* = 1.5, 6.6 Hz, acridine H), 8.05 (d, 1 H, *J* = 8.5 Hz, acridine H), 8.15 (s, 1 H, acridine H), 8.25 (dd, 1 H, *J* = 8.6, 1 Hz, acridine H), 10.21 (s, 1 H, oxime H).

^{13}C NMR ($CDCl_3$ 50 MHz): δ = 19.78 and 21.26 (CH_3), 125.86, 127.07, 127.92, 128.45, 129.00, 129.14, 129.25, 130.81, 131.29, 132.86, 135.37, 135.60, 136.68, 137.10, 138.52, 139.01, 148.53, 149.52 (aromatic C), 160.60 (C=O).

Anal. calcd for $C_{23}H_{20}N_2O$ (340.4) C, 81.15; H, 5.92; N, 8.23. Found: C, 81.21; H, 5.85; N, 8.31.

MS: *m*/*z* = 340 ($M^{+\cdot}$), 339 (M – 1)$^+$, 323 (M – 17)$^+$, 178 (M – 162)$^+$.

Mesityl([1,10]phenanthrolin-5-yl)methanone Oxime (2e)
Yield: 92% by treatment with MeONa; 74% by treatment with $LiAlH_4$; white crystals; mp 246–248 °C.

IR (KBr): ν = 3278, 1610 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.20 (s, 6 H, CH_3), 2.25 (s, 3 H, CH_3), 6.85 (s, 2 H, Mes H), 7.51 (dd, 1 H, *J* = 8.1, 4.5 Hz, phenanthroline H), 7.64 (s, 1 H, phenanthroline H), 7.71 (dd, 1 H, *J* = 8.3, 4.5 Hz, phenanthroline H), 8.07 (dd, 1 H, *J* = 8.1, 1.8 Hz, phenanthroline H), 8.98 (dd, 1 H, *J* = 4.5, 1.6 Hz, phenanthroline H), 9.08 (dd, 1 H, *J* = 4.5, 1.8 Hz, phenanthroline H), 9.65 (dd, 1 H, *J* = 8.3, 1.8 Hz, phenanthroline H), 11.08 (br s, 1 H, oxime H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 20.34 and 21.12 (CH_3), 122.32, 122.93, 125.43, 128.75, 130.91, 131.95, 134.27, 136.79, 137.28, 139.00, 150.16, 150.62 (aromatic C), 159.44 (oxime C).

Anal. calcd for $C_{22}H_{19}N_3O$ (341.4) C, 77.40; H, 5.61; N, 12.31. Found: C, 77.52; H, 5.67; N, 12.37.

MS: *m*/*z* = 341 ($M^{+\cdot}$), 340 (M - 1)$^+$, 324 (M - 17)$^+$, 179 (M - 162)$^+$.

Mesityl([4,7]phenanthrolin-5-yl)methanone Oxime (2f)
Yield: 81% by treatment with MeONa; 75% by treatment with $LiAlH_4$; white crystals; mp 254–255 °C.

IR (KBr): ν = 3282, 1608 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.15 (s, 6 H, CH_3), 2.27 (s, 3 H, CH_3), 6.88 (s, 2 H, Mes H), 7.65 (dd, 1 H, *J* = 4.4, 8.4 Hz, phenanthroline H), 7.74 (dd, 1 H, *J* = 4.6, 8.6 Hz, phenanthroline H), 8.05 (s, 1 H, phenanthroline H), 8.92 (d, 1 H, *J* = 8.5 Hz, phenanthroline H), 9.03 (d, 1 H, *J* = 8.5 Hz, phenanthroline H), 9.05 (d, 1 H, *J* = 4.4 Hz, phenanthroline H), 9.14 (d, 1 H, *J* = 4.4 Hz, phenanthroline H), 11.13 (br s, 1H, oxime H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 20.42 and 21.02 (CH_3), 117.16, 122.06, 122.54, 122.63, 123.52, 128.79, 129.26, 131.84, 134.29, 134.49, 137.30, 149.54, 149.61, 151.12 (aromatic C), 159.78 (oxime C).

Anal. calcd for $C_{22}H_{19}N_3O$ (341.4) C, 77.40; H, 5.61; N, 12.31. Found: C, 77.48; H, 5.69; N, 12.29.

MS: *m*/*z* = 341 ($M^{+\cdot}$), 340 (M – 1)$^+$, 324 (M – 17)$^+$, 179 (M – 162)$^+$.

Mesityl([1,7]phenanthrolin-5-yl)methanone Oxime (2g)
Yield: 87% by treatment with MeONa; 77% by treatment with $LiAlH_4$; white crystals; mp 231–233 °C.

IR (KBr): ν = 3278, 1608 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.20 (s, 6 H, CH_3), 2.25 (s, 3 H, CH_3), 6.85 (s, 2 H, Mes H), 7.51 (dd, 1 H, *J* = 8.1, 4.5 Hz, phenanthroline H), 7.64 (s, 1 H, phenanthroline H), 7.71 (dd, 1 H, *J* = 8.3, 4.5 Hz, phenanthroline H), 8.07 (dd, 1 H, *J* = 8.1, 1.8 Hz, phenanthroline H), 8.98 (dd, 1 H, *J* = 4.5, 1.6 Hz, phenanthroline H), 9.08 (dd, 1 H, *J* = 4.5, 1.8 Hz, phenanthroline H), 9.65 (dd, 1 H, *J* = 8.3, 1.8 Hz, phenanthroline H), 11.08 (br s, 1H, oxime H).

^{13}C NMR ($CDCl_3$ 50 MHz): δ = 20.34 and 21.12 (CH_3), 122.32, 122.93, 125.43, 128.75, 130.91, 131.95, 134.27, 136.79, 137.28, 139.00, 150.16, 150.62 (aromatic C), 159.44 (oxime C).

Anal. calcd for $C_{22}H_{19}N_3O$ (341.4) C, 77.40; H, 5.61; N, 12.31. Found: c, 77.45; H, 5.56; N, 12.39.

MS: *m*/*z* = 341 ($M^{+\cdot}$), 340 (M – 1)$^+$, 324 (M – 17)$^+$, 179 (M – 162)$^+$.

Mesityl([1,7]phenanthrolin-6-yl)methanone Oxime (2h)
Yield: 86% by treatment with MeONa; 70% by treatment with $LiAlH_4$; white crystals; mp 240–242 °C.

IR (KBr): ν = 3276, 1610 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.19 (s, 6 H, CH_3), 2.22 (s, 3 H, CH_3), 6.83 (s, 2 H, Mes H), 7.60 (q, 2 H, phenanthroline H), 7.63 (s, 1 H, phenanthroline H), 8.42 (dd, 1 H, *J* = 8.6, 1.8 Hz, phenanthroline H), 8.91 (dd, 1 H, *J* = 4.6, 1.6 Hz, phenanthroline H), 9.00 (dd, 1 H, *J* = 4.6, 1.6 Hz, phenanthroline H), 9.49 (dd, 1 H, *J* = 7.8, 1.2 Hz, phenanthroline H), 11.10 (br s, 1H, oxime H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 20.39 and 20.80 (CH_3), 121.94, 122.66, 123.46, 127.52, 128.67, 128.82, 129.90, 132.94, 133.38, 137.25, 137.38, 138.54, 149.30, 150.11, 150.94, 151.68 (aromatic C), 162.48 (oxime C).

Anal. calcd for $C_{22}H_{19}N_3O$ (341.4) C, 77.40; H, 5.61; N, 12.31. Found: C, 77.49; H, 5.68; N, 12.35.

MS: *m*/*z* = 341 ($M^{+\cdot}$), 340 (M – 1)$^+$, 324 (M – 17)$^+$, 179 (M – 162)$^+$.

Mesityl(pyren-4-yl)methanone (3a)
Yield: 60% by oxidation with DMP; 80% by reduction with Raney-Ni; white crystals; mp 203–205 °C.

IR (KBr): ν = 1673 (C=O) cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.26 (s, 6 H, CH_3), 2.38 (s, 3 H, CH_3), 6.98 (s, 2 H, Mes H), 7.90–8.27 (m, 8 H, pyrene H), 9.55 (d, 1 H, *J* = 7.8 Hz, pyrene H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 19.93 and 21.15 (CH_3), 124.76, 125.71, 125.95, 126.14, 126.35, 126.49, 126.72, 128.09, 128.70, 129.75, 130.75, 130.96, 131.37, 131.94, 134.76, 135.11, 138.01, 139.73 (aromatic C), 179.74 (C=O).

Anal. calcd for $C_{26}H_{20}O$ (348.5) C, 89.62; H, 5.79. Found: C, 89.79; H, 5.86.

MS: *m*/*z* = 348 ($M^{+\cdot}$), 229 (M – 119)$^+$, 147 (M – 201)$^+$.

Mesityl(9-phenanthryl)methanone (3b)
Yield: 62% by oxidation with DMP; 84% by reduction with Raney-Ni; 82% by reduction with Pd/C; white crystals; mp 171–173 °C.

IR (KBr): ν = 1674 (C=O) cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.22 (s, 6 H, CH_3), 2.35 (s, 3 H, CH_3), 6.94 (s, 2 H, Mes H), 7.54 (t, 1 H, *J* = 7.5 Hz, phenanthrene H), 7.60 (s, 1 H, phenanthrene H), 7.67–7.75 (m, 4 H, phenanthrene H), 8.66 (d, 1 H, *J* = 8 Hz, phenanthrene H), 8.74 (d, 1 H, *J* = 5.5 Hz, phenanthrene H), 9.09 (s, 1 H, phenanthrene H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 19.97 and 21.13 (CH_3), 122.54, 123.04, 126.81, 126.89, 126.97, 127.36, 128.27, 128.83, 129.65, 130.52, 131.23, 130.41, 134.95, 138.40 (aromatic C), 179.78 (C=O).

Anal. calcd for $C_{24}H_{20}O$ (324.4) C, 88.85; H, 6.21. Found: C, 88.91; H, 6.25.

MS: *m*/*z* = 324 ($M^{+\cdot}$), 205 (M – 119)$^+$, 147 (M – 177)$^+$.

Mesityl(1-anthryl)methanone (3c)
Yield: 54% by oxidation with DMP; 78% by reduction with Raney-Ni; white crystals; mp179–181 °C.

IR (KBr): ν = 1660 (C=O) cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.19 (s, 6 H, CH_3), 2.34 (s, 3 H, CH_3), 6.94 (s, 2 H, Mes H), 7.28 (m, 2 H, anthracene H), 7.50 (m, 2 H, anthracene H), 8.06 (m, 3 H, anthracene H), 8.47 (s, 1 H, anthracene H), 9.89 (s, 1 H, anthracene H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 19.80 and 21.09 (CH_3), 123.91, 125.59, 125.91, 127.01, 127.72, 128.56, 128.79, 129.05, 129.24, 131.37, 131.68, 132.38, 132.68, 134.58, 135.03, 137.89, 139.88 (aromatic C), 179.84 (C=O).

Anal. calcd for $C_{24}H_{20}O$ (324.4) C, 88.85; H, 6.21. Found: C, 85.95; H, 6.31.

MS: *m*/*z* = 324 ($M^{+\cdot}$), 205 (M – 119)$^+$, 147 (M – 177)$^+$.

Mesityl(4,5,9,10-tetrahydropyren-4-yl)methanone (6)
Yield 65%; white crystals; mp 161–163 °C.

IR (KBr): ν = 1692 (C=O) cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.09 (s, 6 H, CH_3), 2.28 (s, 3 H, CH_3), 2.87, (m, 4 H, tetrahydropyrene H), 3.21 (m, 2 H, tetrahydropyrene H), 3.91 (dd, 1 H, *J* = 6, 2.4 Hz, tetrahydropyrene H), 6.74–6.89 (m, 2 H, tetrahydropyrene H), 6.96 (s, 2 H, Mes H), 6.98–7.18 (m, 4 H, tetrahydropyrene H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 19.05, 19.74 and 21.26 (CH_3), 28.18, 28.41 and 30.40 (CH_2), 125.77, 126.58, 126.74, 126.888, 127.25, 127.52, 128.00, 129.77, 130.33, 130.87, 132.76, 133.60, 134.72, 135.15, 135.22, 135.34, 137.73 (aromatic C), 197.65 (C=O).

Anal. calcd for $C_{26}H_{24}O$ (352.5) C, 88.60; H, 6.86%. Found: C, 88.62; H, 6.85.

MS: *m*/*z* = 352 ($M^{+\cdot}$), 233 (M – 119)$^+$, 147 (M – 205)$^+$.

1-Mesityl-3a,4,5, 7,8,9,10,11b-octahydroanthra[1,2-*d*]isoxazole (7)
Yield 60%; white crystals; mp 148–150 °C.

IR (KBr): ν = 2925, 2853, 1450, 1380 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.20 (m, 1 H, CH_2), 1.29 (m, 1 H, CH_2), 1.49 (m, 2 H, CH_2), 1.56 (m, 2 H, CH_2), 2.19 (s, 3 H, CH_3), 2.26 (m, 1 H, CH_2), 2.30 (s, 6 H, CH_3), 2.31 (m, 1 H, CH_2), 2.27 (m, 1 H, CH_2), 2.73 (m, 1 H, CH_2), 2.79 (m, 1 H, CH_2), 2.88 (m, 1 H, CH_2), 4.48 (d, 1 H, *J* = 10.6 Hz, isoxazoline H-4), 5.16 (ddd, 1 H, *J* = 10.6, 5.8, 2.8 Hz, isoxazoline H-5), 6.01 (s, 1 H, CH), 6.05 (s, 1 H, Mes H), 6.83 (s, 1 H, CH), 6.85 (s, 1 H, Mes H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 18.52, 19.80, 21.10 (CH_3), 23.15, 23.85, 28.72, 28.97, 29.68 (CH_2), 53.75 (C-4 isoxazoline), 78.69 (C-5 isoxazoline), 125.60, 126.93, 128.03, 129.00, 135.06, 135.36, 135.37, 135.89, 138.32 (aromatic C), 159.08 (C=N).

Anal. calcd for $C_{24}H_{27}NO$ (345.5) C, 83.44; H, 7.88; N, 4.05. Found: C, 83.52; H, 7.81; N, 4.09.

MS: *m*/*z* = 345 ($M^{+\cdot}$), 198 (M – 147)$^+$, 184 (M – 161)$^+$, 161 (M – 184)$^+$, 147 (M – 198)$^+$.

Acknowledgement

The authors are grateful to the E.U. from INTAS and Italian M.U.R.S.T. for financial support.

References

(1) Caramella, P.; Grünanger, P. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984, Vol. 1, p 291.
(2) Corsaro, A.; Pistarà V. In *Trends in Heterocyclic Chemistry*; 1995, *4*, 169.
(3) Corsaro, A.; Librando, V.; Chiacchio, U.; Pistarà, V. *Tetrahedron* **1996**, *52*, 13027.
Librando, V.; Chiacchio, U.; Corsaro, A.; Gumina, G. *Polycyclic Arom. Compds.* **1996**, *11*, 313.
(4) Corsaro, A.; Librando, V.; Chiacchio, U.; Pistarà, V.; Rescifina, A. *Tetrahedron* **1998**, *54*, 9187.
(5) Corsaro, A.; Chiacchio, U.; Librando, V.; Fisichella, S.; Pistarà, V. *Heterocycles* **1997**, *45*, 1567.
(6) Desimoni, G.; Faita, G. In *Seminars in Organic Synthesis, XVI Summer Scool "A.Corbella"*; Polo Editoriale Chimico, 1991, p 4, 9.
Grünanger, P.; Vita Finzi, P. In *The Chemistry of Heterocyclic Compounds*; Taylor E. C. Ed.; Wiley Interscience: New York, 1991, Chapter 2.
Chiacchio, U.; Rescifina, A.; Romeo, G. In *Targets in Herocyclic Systems*; Attanasi, O. A.; Spinelli, D., Eds.; SCI: Roma, 1997, Vol. 1, p 225.
(7) Corsaro, A.; Chiacchio, U.; Pistarà, V.; Rescifina, A., unpublished results.
(8) Dess, D. B.; Martin, J. C. *J. Org. Chem*. **1983**, *48*, 4155.
(9) Gore, P. M. *Chem. Rev*. **1955**, *55*, 229.
Olah, G. A. In *Friedel-Crafts and Related Reactions*; Wiley Interscience: New York, 1963–1964, Vol. 1-4.
Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964, Vol. 1.
(10) Gore, P. M.; Hoskins, J. A. *J. Chem. Soc*. **1964**, 5666.

Article Identifier:
1437-210X,E;2000,0,10,1469,1473,ftx,en;Z01000SS.pdf