

SHORT
COMMUNICATIONSReaction of 10-(4-Tolylsulfonyloximino)phenanthren-9-one
with Aromatic Amines, Hydrazines, and HydrazidesA. P. Stankvichyus^a, L. N. Yanushene^a, and V. E. Skiryus^b^a Institute of Cardiology, Kaunas Medical University, pr. Sukilelyu 17, Kaunas, 50009 Lithuania
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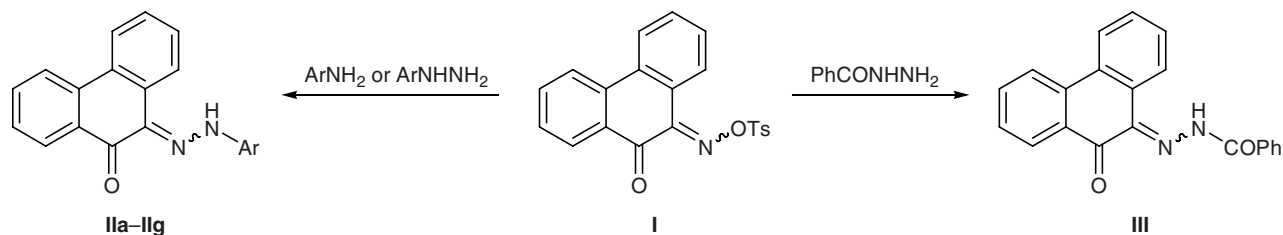
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We found previously that aliphatic amines smoothly react with phenanthrene-9,10-quinone *O*-(*p*-tolylsulfonyl)oxime (**I**) on cooling to give 2-(2'-cyanophenyl)-benzamide in a good yield. However, in the reaction of **I** with 4-methylaniline, instead of the expected anilide, we isolated phenanthrene-9,10-quinone 9-(4-methylphenylhydrazono). The same product was obtained in good yield by heating compound **I** with 4-methylphenylhydrazine [1]. In the present communication we report on the reactions of *O*-(4-methylphenylsulfonyl)oxime **I** with aromatic amines and arylhydrazines having various substituents in the aromatic ring. In all cases no amides were obtained, but the corresponding hydrazones **IIa–IIe** were formed. In the reaction with 2,4-dinitroaniline we detected only traces of hydrazone **IIg** (by chromatography). These data indicate that the formation of the –N=N– bond is hindered in reactions with aromatic amines having electron-withdrawing substituents and that the effect of the *ortho*-substituent is insignificant. By reactions of compound **I** with arylhydrazines we obtained hydrazones **IIc**, **IId**, and **IIf** in good yields, while the yield of 2,4-dinitrophenylhydrazone **IIg** reached 92%. Benzohydrazide reacted with oxime ester **I** to give 43% of benzoylhydrazone **III**.

10-(4-Tolylsulfonyloximino)-9,10-dihydrophenanthren-9-one (I) was synthesized according to the procedure described in [1].

10-(4-Methoxyphenylhydrazono)-9,10-dihydrophenanthren-9-one (IIa). Compound **I**, 1.13 g (3 mmol), was added to a solution of 0.68 g (6 mmol) of 4-methoxyaniline in 5 ml of acetonitrile, and the mixture was stirred until it became homogeneous, left to stand for 2 days at room temperature, and heated for 30 min at 80°C. The solution was diluted with 20 ml of water and stirred, and the precipitate was filtered off, washed with water, and recrystallized from acetic acid with addition of charcoal. Yield 0.67 g (68%), mp 248–249°C [2], *R*_f 0.64 (benzene–hexane–acetonitrile, 2:2:1).

10-(2-Methoxyphenylhydrazono)-9,10-dihydrophenanthren-9-one (IIb). A mixture of 0.758 g (2 mmol) of compound **I** and 1 ml of 2-methoxyaniline in 6 ml of acetonitrile was heated for 3 h under reflux (water bath). The precipitate was filtered off and recrystallized from acetic acid. Yield 0.18 g (27%), mp 252°C, *R*_f 0.60 (benzene–heptane–ethyl acetate, 4:4:1). Mass spectrum, *m/z* (*I*_{rel}, %): 298 (35) [*M*]⁺, 270 (9), 206 (47), 193 (32), 178 (100), 165 (86), 92



II, Ar = 4-MeOC₆H₄ (**a**), 2-MeOC₆H₄ (**b**), 2-MeC₆H₄ (**c**), 3-MeC₆H₄ (**d**), 2-Me-4-O₂NC₆H₃ (**e**), 4-O₂NC₆H₄ (**f**), 2,4-(O₂N)₂C₆H₃ (**g**).

(51), 77 (30). Found, %: C 76.58; H 4.61; N 8.37. $C_{21}H_{16}N_2O_2$. Calculated, %: C 76.83; H 4.88; N 8.52.

10-(2-Methylphenylhydrazono)-9,10-dihydrophenanthren-9-one (IIc). *a.* A mixture of 1.13 g (3 mmol) of compound **I** and 5 ml of 2-methylaniline (excess) was kept for 4 days at room temperature. Yield of **IIc** 0.31 g (33%), mp 225–226°C (from acetic acid); published data [2]: mp 222–223°C; R_f 0.36 (benzene–hexane, 3:2).

b. A mixture of 0.75 g (2 mmol) of compound **I** and 0.49 g (4 mmol) of (2-methylphenyl)hydrazine in 10 ml of acetonitrile was heated for 20 min under reflux. The mixture was cooled, diluted with 20 ml of water, and acidified with dilute hydrochloric acid (1:1) to pH 5.5–6.0. The product was recrystallized from acetic acid. Yield 0.38 g (61%), mp 225–226°C, R_f 0.36 (benzene–heptane, 3:2).

10-(3-Methylphenylhydrazono)-9,10-dihydrophenanthren-9-one (IId). *a.* Compound **IId** was synthesized from 1.89 g (5 mmol) of oxime **I** and 8 ml of 3-methylaniline as described above for hydrazone **IIc** (method *a*). Yield 0.54 g (35%), mp 148–149°C (from acetic acid), R_f 0.72 (benzene–heptane–ethyl acetate, 4:4:1). Found, %: C 80.46; H 4.89; N 8.65. $C_{21}H_{16}N_2O$. Calculated, %: C 80.77; H 5.12; N 8.97.

b. A mixture of 0.75 g (2 mmol) of compound **I** and 1 ml of (3-methylphenyl)hydrazine in 8 ml of acetic acid was heated for 5 min under reflux. The mixture was cooled, and the precipitate was filtered off. Yield 0.45 g (72%), mp 148–149°C (from acetic acid), R_f 0.72 (benzene–heptane–ethyl acetate, 4:4:1). Mass spectrum, m/z (I_{rel} , %): 312 (43) [M]⁺, 234 (6), 206 (43), 193 (37), 178 (80), 165 (100), 106 (89), 91 (18).

10-(2-Methyl-4-nitrophenylhydrazono)-9,10-dihydrophenanthren-9-one (IIe). A mixture of 1.13 g (3 mmol) of compound **I** and 0.91 g (6 mmol) of 2-methyl-4-nitroaniline in 10 ml of acetonitrile was heated for 3 h under reflux. The mixture was diluted with 20 ml of water and cooled, and the precipitate was filtered off and recrystallized from acetic acid. Yield 0.29 g (27%), mp 263–265°C (from acetic acid), R_f 0.8 (benzene–hexane–acetonitrile, 2:2:1). Mass spectrum, m/z (I_{rel} , %): 357 (32) [M]⁺, 329 (12), 206 (53), 193 (37), 178 (80), 165 (100), 151 (67), 136 (18). Found, %: C 70.33; H 4.04; N 11.89. $C_{21}H_{15}N_3O_3$. Calculated, %: C 70.59; H 4.20; N 11.76.

10-(4-Nitrophenylhydrazono)-9,10-dihydrophenanthren-9-one (IIf). A mixture of 0.38 g (1 mmol) of compound **I** and 0.36 g (2 mmol) of 4-nitrophenylhydrazine in 10 ml of acetonitrile was heated for 20 min under reflux. Yield of hydrazone **IIf** 0.13 g (38%), mp 249–250°C (from acetic acid) [3], R_f 0.61 (ethyl acetate–carbon tetrachloride, 3:1).

10-(2,4-Dinitrophenylhydrazono)-9,10-dihydrophenanthren-9-one (IIg). A mixture of 0.75 g (2 mmol) of compound **I** and 1 g (5 mmol) of 2,4-dinitrophenylhydrazine in 10 ml of acetonitrile was heated for 20 min under reflux. The mixture was diluted with 20 ml of water and acidified with dilute hydrochloric acid (1:1) to pH 5.5–6.0, and the precipitate was filtered off and recrystallized from acetic acid with addition of charcoal. Yield 0.72 g (92%), mp 334–336°C [2], R_f 0.11 (benzene–heptane, 3:2). Mass spectrum, m/z (I_{rel} , %): 388 (24) [M]⁺, 360 (20), 206 (59), 193 (67), 182 (41), 178 (88), 167 (12), 165 (100).

***N'*-(10-Oxo-9,10-dihydrophenanthren-9-ylidene)-benzohydrazide (III).** A mixture of 0.62 g (6 mmol) of benzohydrazide and 0.75 g (2 mmol) of compound **I** in 10 ml of anhydrous ethanol was heated for 7 h under reflux. The mixture was diluted with 20 ml of water, and the precipitate was filtered off and recrystallized from acetonitrile with addition of charcoal. Yield 0.28 g (43%), mp 195–196°C [4], R_f 0.47 (ethyl acetate–carbon tetrachloride, 1:3).

The purity of the products was checked by TLC on Silufol UV-254 plates; spots were detected by treatment with iodine vapor. The mass spectra (electron impact, 70 eV) were recorded on a Finigan MAT-212 mass spectrometer with direct sample admission into the ion source.

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