

SHORT
COMMUNICATIONS

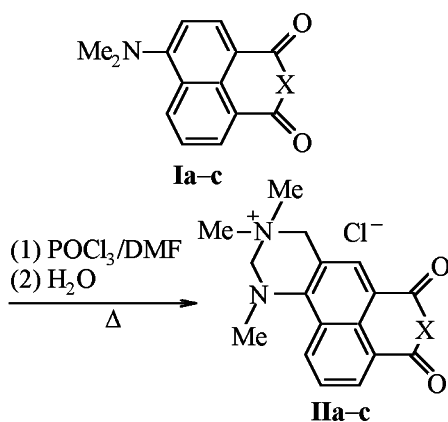
Behavior of 2-Phenyl-2,3-dihydro-1*H*-1,3-phenalenediones in Formylation by Vilsmeier–Haak Procedure

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We discovered formerly [1, 2] that at heating 4-dimethylamino-substituted imines and anhydride of naphthalic acid **Ia–c** with POCl₃ and DMF (under conditions of Vilsmeier–Haak reaction) instead of expected 3-formyl derivatives arose quinazolinium salts **IIa–c**.

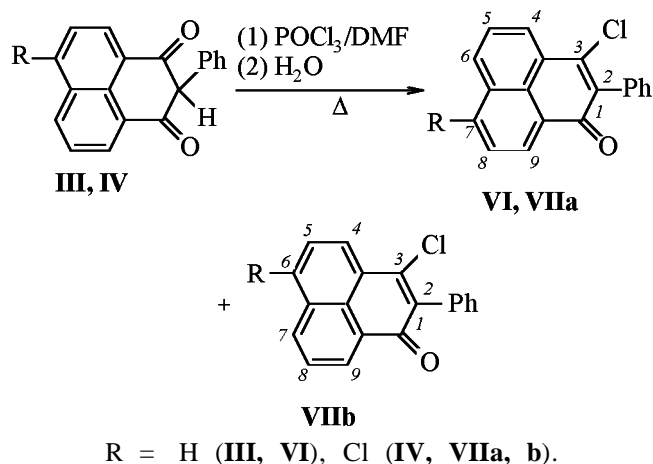


X = NAr (a), NMe (b), O (c).

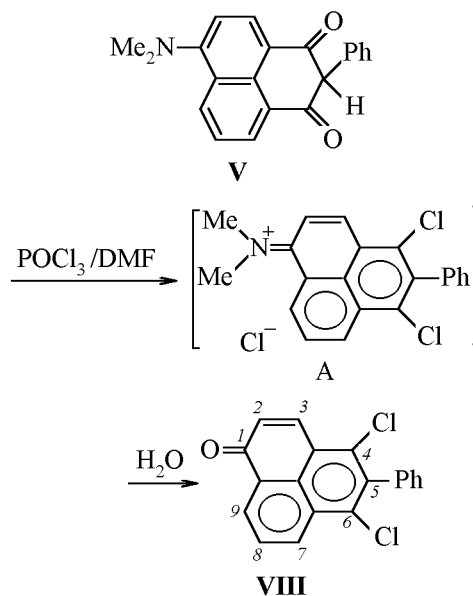
In extension of these investigations we studied the reaction with Vilsmeier complex of 2-phenyl-2,3-dihydro-1*H*-1,3-phenalenedione (**III**), and also its 6-chloro (**IV**) and 6-dimethylamino (**V**) derivatives.

It was found that compound **III** readily reacted with POCl₃ and DMF at 20°C and within 40 min was completely converted into 3-chloro-2-phenyl-1*H*-1-phenalenedione (**VI**). The chlorine-substituted compound **IV** began to react at 35°C and within 25 min formed an equimolar mixture of isomeric 3,7-dichloro- (**VIIa**) and 3,6-dichloro- (**VIIb**) 2-phenyl-1*H*-1-phenalenediones.

However the dimethylamino-substituted compound **V** under similar conditions (35°C, 30 min) unexpectedly furnished 4,6-dichloro-5-phenyl-1*H*-1-



phenalenedione (**VIII**). Apparently the reaction proceeds via iminium salt **A** formation, and the latter is hydrolyzed at treating the reaction mixture with water.



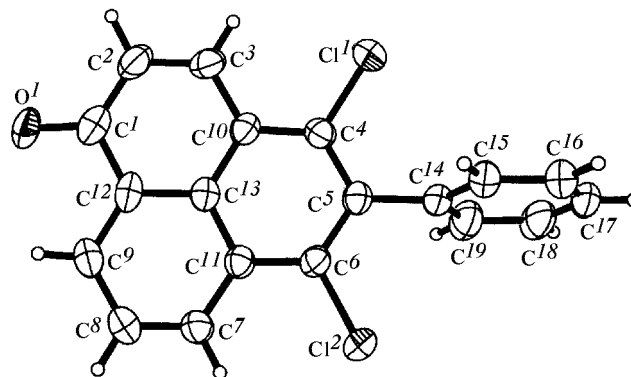
The structure of all compounds synthesized **III–VIII** was confirmed by ^1H NMR spectra, and that of phenalene **VIII** also by X-ray diffraction analysis (see figure).

2-Phenyl-3-chloro-1H-1-phenalene (VI). Yield 74%, mp 147–147.5°C. ^1H NMR spectrum, (δ , ppm): 8.49 d.d (1H, H^9 , J_1 8.3, J_2 1.0 Hz), 8.47 d (1H, H^4 , J 8.3 Hz), 8.41 d.d (1H, H^7 , J_1 8.3, J_2 1.0 Hz), 8.35 d (1H, H^6 , J 8.3 Hz), 7.91 t (1H, H^5 , J 7.8 Hz), 7.83 t (1H, H^8 , J 7.8 Hz), 7.31–7.53 m (5H, arom). Found, %: C 78.41; H 3.67; Cl 12.24. $\text{C}_{19}\text{H}_{11}\text{ClO}$. Calculated, %: C 78.49; H 3.79; Cl 12.22.

2-Phenyl-3,7-dichloro-1H-1-phenalene (VIIa). ^1H NMR spectrum, (δ , ppm): 8.66 d (1H, H^6 , J 8.3 Hz), 8.58 d.d (1H, H^4 , J_1 7.4, J_2 1.0 Hz), 8.32 d (1H, H^3 , J 8.1 Hz), 8.04 d (1H, H^8 , J 8.0 Hz), 8.03 d.d (1H, H^5 , J_1 8.0, J_2 0.7 Hz), 7.29–7.57 m (5H arom). Found, %: C 70.10; H 3.07; Cl 21.84. $\text{C}_{19}\text{H}_{10}\text{Cl}_2\text{O}$. Calculated, %: C 70.15; H 3.08; Cl 21.85.

2-Phenyl-3,6-dichloro-1H-1-phenalene (VIIb). ^1H NMR spectrum, (δ , ppm): 8.52 d (1H, H^7 , J 8.1 Hz), 8.48 d (1H, H^9 , J 7.4 Hz), 8.43 d (1H, H^4 , J 8.1 Hz), 7.97 d (1H, H^5 , J 8.0 Hz), 7.95 t (1H, H^8 , J 8.1 Hz), 7.29–7.57 m (5H arom). Found, %: C 70.10; H 3.07; Cl 21.84. $\text{C}_{19}\text{H}_{10}\text{Cl}_2\text{O}$. Calculated, %: C 70.15; H 3.08; Cl 21.85.

5-Phenyl-4,6-dichloro-1H-1-phenalene (VIII). Yield 78%, mp 273–274°C. ^1H NMR spectrum, (δ , ppm): 8.73 d.d (1H, H^9 , J_1 8.4, J_2 1.1 Hz), 8.61 d.d (1H, H^7 , J_1 8.5, J_2 1.1 Hz), 8.30 d (1H, H^4 , J 10.1 Hz), 8.06 d.d (1H, H^8 , J_1 8.5, J_2 1.1 Hz), 7.33–7.68 m (5H arom), 6.83 d (1H, H^5 , J 10.1 Hz). Found, %: C 70.01; H 3.01; Cl 21.54. $\text{C}_{19}\text{H}_{10}\text{Cl}_2\text{O}$. Calculated, %: C 70.15; H 3.08; Cl 21.85. Data of X-ray study: space group $\text{P}\bar{1}$ at 17°C, a 7.029(1), b 10.144(2), c 10.310(2) Å, α 82.38(1)°, β 81.26(1)°, γ 80.11(1)°, V 711.6(2) Å³, Z 2, R 0.0386.



Spatial structure of phenalene **VIII** molecule according to the data of X-ray diffraction analysis.

The reaction progress was monitored and the purity of compounds obtained was checked by TLC on Sorbfil PTLC-AF-A-UV plates, eluent for phenalones **VI** and **VIIa, b** hexane–benzene, 2:1, for phenalene **VIII** chloroform–ethanol, 20:1. ^1H NMR spectra were registered on spectrometer Varian Mercury-VX-200 (operating frequency 200 MHz) from solutions in $\text{DMSO}-d_6$, internal reference TMS.

Initial compounds **III–V** were synthesized by procedures described in [3, 4]. Their melting point corresponded to the published values.

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