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LETTERS TO THE EDITOR

Synthesis of Triphenylphosphazoperiindenones by Staudinger Reaction

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We have reported earlier [1] on the synthesis of new iminophosphorane dyes on the basis of amino derivatives of phenalenone abd benzanthrone along the schemes of Appel and Kirsanov reactions. The compounds obtained are substances with intensive luminescence, and some of them are promising as dyes for quantum electronics.

This communication reports on the alternative pathway to the triphenylphosphazo compounds on the basis of periindenones by the method of Staudinger [2].

Initial 6-aminophenalenone (Ia), 3-amino-2-phenylphenalenone (IIa), and 3-aminobenzanthrone (IIIa) were transformed into the corresponding azidoderivatives **Ib–IIIb** by the procedure resembling that described in [3], and then under mild conditions they were brought into the reaction with triphenylphosphine. The scheme below shows these transformations by the example of compound Ia.



Synthesis of **IIa** was carried out from the corresponding 3-hydroxyphenalenone by the procedure close to that described in [4].

The following systems were used for thin layer chromatography: chloroform–ethanol, 10:1 (1), chloro-form–acetone, 331:169 (2) and benzene–dioxane, 88:12 (3). IR spectra were registered on a Fourier spectrometer FSM-1201, the ³¹P NMR spectra were registered on a Bruker WO-80SY instrument with operating frequency 32.4 MHz, relative to 85% H₃PO₄.

6-Azido-1H-phenalen-1-one (Ib). A suspension of 1.95 g (0.01 mol) of 6-aminopenalenone and 4 ml (0.07 mol) of conc. H₂SO₄ in 10 ml of acetic acid at stirring and cooling to -5°C was treated with a solution of 0.76 g (0.07 mol) of sodium nitrite in 5 ml of water. The stirring was continued for 5 min and then a solution of 0.25 g (0.04 mol) of sodium azide in 5 ml of water was added dropwise, and the mixture was stirred for 2 h at cooling. Then 25 ml of cold water was added, the precipitate was filtered off, washed with water to neutral reaction, and dried in a vacuum. The product was purified by chromatography on silica gel (eluent chloroform), the process of separation was monitored by TLC. After removing the solvent, yellow crystals were obtained, mp 170-172°C. IR spectrum (KBr): 2110 cm⁻¹ (N₃). Yield 1.48 g (72%), R_f 0.78 (1), 0.86 (2), 0.57 (3). Found, %: N 18.78, 18.41. C₁₃H₇N₃O. Calculated, %: N 18.99.

Other azides were prepared similarly to **Ib** (compound, yield, %, mp, R_f): **IIb**, 78, 168–169°C (aqueous alcohol), 0.78 (1), 0.64 (2), 0.73 (3); **IIIb**, 74, –, 0.78 (1), 0.56 (2), 0.93 (3).

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6-Triphenylphosphazo-1*H***-phenalen-1-one** (Ic). To a solution of 1.11 g (5 mmol) of azide Ib in 25 ml of methylene chloride was added dropwise at stirring 1.5 g (5.7 mmol) of triphenylphosphine in 25 ml of methylene chloride. The mixture was heated under reflux for 1 h, then the solvent was removed in a vacuum and the residue was heated with 40 ml of hexane for removing triphenylphosphine excess. The crude product was chromatographed on silica gel (eluent chloroform). Cherry-red crystals, yield 1.78 g (78%), mp 155–156°C. ³¹P NMR spectrum, δ_P 8.25 ppm (ethanol), R_f 0.72 (1), 0.83 (2), 0.45 (3). Found, %: C 80.32, 80.58; H 4.35, 4.46; P 6.23, 6.31; N 2.96, 2.73. C₃₁H₂₂NOP. Calculated, %: C 81.74; H 4.87; P 6.8; N 3.08.

Under analogous conditions were obtained other phosphazo compounds (compound, yield, %, mp, R_f): **IIc**, 69, 154–155°C, 0.52 (1), 0.82 (2), 0.48 (3); **IIIc**, 74, 139–141°C, 0.48 (1), 0.72 (2), 0.44 (3).

All the synthesized compounds showed satisfactory elemental analyses. In the IR spectra of azides **Ib–IIIb** a strong absorption in the region of 2100 cm⁻¹ (N₃) is

registered, in the ³¹P NMR spectra of imines **Ic–IIIc** typical singlet signals appeared in the region of 7–9 ppm.

We failed to carry out similar sequence of transformations for 3-amino-1-phenalenone IVa. This is consistent with the data of [4] mentioning that this compound like many other β -dicarbonyl compounds [5] do not form diazo compounds in the reaction with sodium nitrite.

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