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Retention of a six-membered ring in the reaction of 2-dialkylaminobenzo[*e*]-1,3,2-dioxaphosphinin-4-ones with pentafluorobenzaldehyde: O,N-exchange at phosphorus

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General. All of the experiments were performed in an atmosphere of argon. The melting points were measured on a Boethius apparatus (Germany). The NMR spectra were obtained in 5 mm ampoules using Varian-UNITY-300 and Bruker-400 instruments. The values of δ_H, δ_C, and δ_P were determined with reference to the signals of residual protons, the carbon of a deuterated solvent, or an external standard (H_3PO_4). The values of δ_F were determined with reference to an internal standard (C_6F_6) and then converted with respect to $CFCl_3$. The IR spectra were recorded on a Bruker Vector 22 FTIR instrument using KBr pellets or a suspension in Vaseline oil. The EI mass spectra were measured on a TRACE MS Finnigan MAT instrument; the ionization energy was 70 eV, and the ion source temperature was 290°C. The samples were introduced into the ion source by direct injection. The sample with an ampoule was heated from 100 to 350°C under temperature-programmed conditions. The mass spectra were obtained with the use of the Xcalibur software.

^{13}C NMR spectrum for compound **4a** (DMSO-d_6, δ_C ppm; J Hz) (henceforth, the shape of a signal in the ^{13}C-{^1H} NMR spectrum is given in parentheses): 167.56 br d (s) (C^4, $^3J_{HC^5CC^4}$ 4.1), 150.37 br d d d (d) (C^{8a}, $^3J_{HC^5CC^{8a}}$ 7.5-8.0, $^3J_{HC^7CC^{8a}}$ 7.5-8.0, $^2J_{POC^{8a}}$ 7.5), 145.01 d m (d m) (C^{11}, $^1J_{FC^{11}}$ 248.0, $^2J_{FC^{12}C^{11}}$ 10.0-12.0, $^3J_{PCCC^{11}}$ 7.0-8.0), 140.25 d m (d m) (C^{13}, $^1J_{FC^{13}}$ 252.9, $^2J_{FC^{12}C^{13}}$ 11.0-12.0), 136.93 d m (d m) (C^{12}, $^1J_{FC^{12}}$ 249.8, $^2J_{FC^{11}C^{12}}$ 12.5, $^2J_{FC^{13}C^{12}}$ 12.5), 132.00 d d (s) (C^7, $^1J_{HC^7}$ 161.7, $^3J_{HC^5CC^7}$ 9.0), 130.56 d d (s) (C^5, $^1J_{HC^5}$ 162.0, $^3J_{HC^7CC^5}$ 7.4), 124.30 br m (br d) (C^{4a}, $^3J_{POCC^{4a}}$ 5.5), 122.59 d d (s) (C^6, $^1J_{HC^6}$ 162.2, $^3J_{HC^8CC^6}$ 6.9), 121.96 d d m (d) (C^8, $^1J_{HC^8}$ 164.1, $^3J_{HC^6CC^8}$ 7.5, $^3J_{POCC^8}$ 2.0), 109.19 m (m) (C^{10}, $^2J_{FC^{11}C^{10}}$ 16.8, $^2J_{PCC^{10}}$ 7.3, $^3J_{FC^{12}CC^{10}}$ 4.0), 55.11 br d d (br d) (C^9, $^1J_{PC^9}$ 135.0-136.0, $^1J_{HC^9}$ 136.0-137.0), 46.11 br t (br s) (C^{16}, $^1J_{HC^{16}}$ 142.5), 9.21 br q (br s) (C^{17}, $^1J_{HC^{17}}$ 125.7).

^{13}C NMR spectrum for compound **4b** (DMSO-d_6, δ_C ppm; *J* Hz): 167.16 br d (s) (C^4, $^3J_{HC^5CC^4}$ 4.3), 150.87 br d d d (d) (C^{8a}, $^3J_{HC^5CC^{8a}}$ 8.5, $^3J_{HC^7CC^{8a}}$ 8.5, $^2J_{POC^{8a}}$ 7.7), 145.28 d m (d m) (C^{11}, $^1J_{FC^{11}}$ 248.7, $^2J_{FC^{12}C^{11}}$ 10.0-12.0, $^3J_{PCCC^{11}}$ 7.0-8.0), 140.86 d m (d m) (C^{13}, $^1J_{FC^{13}}$ 254.8, $^2J_{FC^{12}C^{13}}$ 17.4), 137.29 d m (d m) (C^{12}, $^1J_{FC^{12}}$ 250.2, $^2J_{FC^{11}C^{12}}$ 14.7, $^2J_{FC^{13}C^{12}}$ 14.7), 132.94 d d (s) (C^7, $^1J_{HC^7}$ 162.0, $^3J_{HC^5CC^7}$ 8.5), 130.95 d d (s) (C^5, $^1J_{HC^5}$ 163.1, $^3J_{HC^7CC^5}$ 4.9-5.0), 123.81 d d d d (d) (C^{4a}, $^3J_{HC^6CC^{4a}}$ 9.1-9.2, $^3J_{HC^8CC^{4a}}$ 9.1-9.2, $^3J_{POCC^{4a}}$ 5.1, $^2J_{HC^5C^{4a}}$ 3.2), 123.31 br d m (s) (C^6, $^1J_{HC^6}$ 163.0, $^3J_{HC^8CC^6}$ 7.7), 122.17 br d d (d) (C^8, $^1J_{HC^8}$ 164.6, $^3J_{HC^6CC^8}$ 7.7, $^3J_{POCC^8}$ 1.5), 107.23 m (m) (C^{10}, $^2J_{FC^{11}C^{10}}$ 17.4), 58.45 br d d (br d) (C^9, $^1J_{PC^9}$ 142.0, $^1J_{HC^9}$ 139.0), 52.17 br t (br d) (C^{16}, $^1J_{HC^{16}}$ 143.1, $^3J_{PCNC^{16}}$ 4.9), 63.88 br t (br s) (C^{17}, $^1J_{HC^{17}}$ 146.0).