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SHORT COMMUNICATIONS

Synthesis of Dimethylphosphorothiol Derivatives of Dibenzo-*p*-dioxin, Phenoxazine, and Phenoxathiyne

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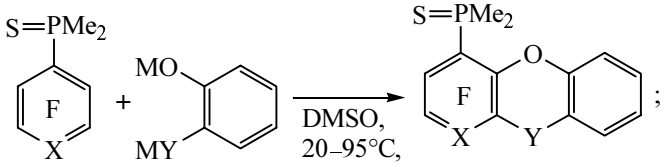
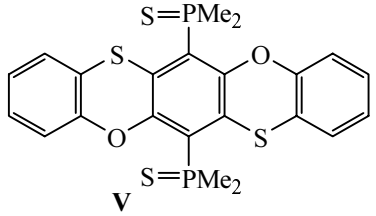
Recently synthesized [1] polyfluoroarylthiophosphines 1-P(S)Me_2-4-XC_6F_4 [X = CF_3, P(S)Me_2, Cl] θ 4-P(S)$Me_2C_5NF_4$ are promising compounds for preparation therefrom potentially biologically active phosphorus-containing substances, in particular, dibenzo-*p*-dioxin derivatives [2]. We demonstrated the possibility of synthesizing heterocycles **I–V** along the scheme:



I–IV



V

I, X = C–CF_3, Y = O; **II**, X = C–Cl, Y = O; **III**, X = N, Y = O; **IV**, X = C–$PSMe_2$, Y = NH; M = Na, Li.

Dioxins **I–III** were prepared by reaction of pyrocatechol disodium salt or 2-aminophenol dilithium salt with the mentioned substrates in 80, 70, and 79% yield respectively. Phenoxazine **IV** was obtained similarly in 35% yield. The reaction between equimolar amounts of 1,4-$(PSMe_2)_2$–C_6F_4 and 2-thiophenol disodium salt afforded at once dioxadithiapentacene (**V**) (90%) (cf. [3]). The salts mentioned were obtained from pyrocatechol, 2-thiophenol, and 2-aminophenol (0.17–0.33 mmol) and MeONa in MeOH or BuLi in heptane respectively. The solvent was removed in a vacuum (0.1 mm Hg.) at 70°C, was added DMSO (2 ml), substrate (0.16–0.30 mmol), and the mixture was stirred for 2 h at 20°C (at 95 and 75°C for **II** and **V** respectively). Then 5 ml of water was added, the precipitate was filtered off, washed with water, dried in air, dissolved in 1 ml of $CHCl_3$, precipitated with pentane (5 ml), and dried in a vacuum. Phenoxazine **IV** was isolated from the reaction mixture by TLC on Silufol plates, eluent $CHCl_3$.

1-Dimethylphosphorothioyl-4-trifluoromethyl-2,3-difluorodibenzo-*p*-dioxin (I). mp 206–207°C. ^{1}H NMR spectrum, δ, ppm: 6.8–7.1 (4H, CH); 2.22 d.d (6H, CH_3, $^2J_{PH}$ 16.6, $^5J_{FH}$ 2.9 Hz). ^{19}F NMR spectrum, δ, ppm: –135.0 d.m (1F, CF, $^3J_{FF}$ 23.3 Hz); –143.3 q.d.d (1F, CF, $^4J_{FF}$ ~27, $^3J_{FF}$ ~23, $^4J_{PF}$ ~4 Hz); –58.0 d (3F, CF_3, $^4J_{FF}$ 26.9 Hz). ^{31}P NMR spectrum, δ, ppm: 30.1 m. Found, %: C 47.06; H 2.37; F 25.04. $C_{15}H_{10}F_5O_2PS$. Calculated, %: C 47.38; H 2.65; F 24.98.

1-Dimethylphosphorothioyl-4-chloro-2,3-difluorodibenzo-*p*-dioxin (II). mp 204–206°C. ^{1}H NMR spectrum, δ, ppm: 6.8–7.1 (4H, CH); 2.21 d.d (6H, CH_3, $^2J_{PH}$ 13.7, $^5J_{FH}$ 3.0 Hz). ^{19}F NMR spectrum, δ, ppm: –135.8 d.m (1F, CF, $^3J_{FF}$ ~ 23 Hz); –143.1 d.d (1F, CF, $^3J_{FF}$ 23.3, $^4J_{PF}$ 3.6 Hz). ^{31}P NMR spectrum, δ, ppm: 29.5 m. Found, %: C 48.45; H 3.27; Cl 10.05; F 10.49.

$C_{14}H_{10}ClF_5O_2PS$. Calculated, %: C 48.50; H 2.91; Cl 10.23; F 10.96.

1-Dimethylphosphorothioyl-2,3-difluoropyridino-5,6-benzo-*p*-dioxin (III). mp 202–204°C. ^{1}H NMR spectrum, δ, ppm: 6.9–7.1 (4H, CH); 2.23 d.d (6H, CH_3, $^2J_{PH}$ 13.7, $^5J_{FH}$ 2.9 Hz). ^{19}F NMR spectrum, δ, ppm: –139.8 m (1F, CF); –94.4 d.d (1F, CF, $^3J_{FF}$ 25.1, $^4J_{PF}$ 5.4 Hz). ^{31}P NMR spectrum, δ, ppm: 29.7 m. Found, %: C 49.77; H 3.23; F 11.99. $C_{13}H_{10}F_2O_2NPS$. Calculated, %: C 49.84; H 3.22; F 12.13.

1,4-Bis(dimethylphosphorothioyl)-2,3-difluorophenoxazine (IV). mp 189–194°C. ^{1}H NMR spectrum, δ, ppm: 10.17 s (1H, NH); 6.4–6.9 (4H, CH); 2.0–2.3 (12H, CH_3). ^{19}F 1NMR spectrum, δ, ppm: –133.7 d (1F, CF, $^3J_{FF}$ ~25 Hz); –141.8 d (1F, CF, $^3J_{FF}$ ~25 Hz). ^{31}P{^{1}H} NMR spectrum, δ_P, ppm: 31.0 d.d (1P, CP, $^3J_{PF}$ 5.2, $^4J_{PF}$ 3.2 Hz); 28.9 t (1P, CP, $^3J_{PF}$ ~ $^4J_{PF}$ ~5.0 Hz). Found: M^+ 403.0158. $C_{16}H_{17}F_2OP_2S_2$. Caltd.: *M* 403.0195.

6,13-Bis(dimethylphosphorothioyl)-5,12-dioxa-7,14-dithiapentacene (V). mp. 260–265°C. ^{1}H NMR spectrum, δ, ppm: 7.0–7.5 (8H, CH); 2.46 d (12H, CH_3, $^2J_{PH}$ 13.4 Hz). ^{31}P{^{1}H} NMR spectrum, δ_P, ppm: 33.3 s. Found: M^+ 505.9847. $C_{22}H_{20}O_2P_2S_4$. Caltd.: *M* 505.9822.

NMR spectra were registered on spectrometer Bruker AC- 200 at operating frequencies 200.13 (^{1}H), 188.31 (^{19}F), and 81.02 (^{31}P) MHz in $CDCl_3$ (δ_H 7.25 ppm.), external references CCl_3F and 85% H_3PO_4. Mass spectra were measured on Varian MAT 212 instrument.

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