

Interaction of 1,3,2,4-Benzodithiadiazines with Aromatic Phosphines and Phosphites

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Received 19 December 2013; revised 11 June 2014

ABSTRACT: Although an interaction between hydrocarbon and fluorocarbon 1,3,2,4-benzodithiadiazines (**1**) and $P(C_6H_5)_3$ continuously produces chiral 1,2,3-benzodithiadiazol-2-yl iminophosphoranes (**2**; in this work, 5,7-difluoro derivative **2a**) via 1:1 condensation, an interaction between **1** and other PR_3 reagents gives different products. With $R = OC_6H_5$ and both hydrocarbon and fluorocarbon **1**, only $X=P(OC_6H_5)_3$ ($X = S, O$) were identified in the complex reaction mixtures by ^{13}C and ^{31}P NMR and GC-MS. With $R = C_6F_5$, no interaction with the archetypal **1** was observed but catalytic addition of atmospheric water to the heterocycle afforded 2-amino-*N*-sulfinylbenzenesulfenamide (**4**). With electrophilic $B(C_6F_5)_3$ instead of nucleophilic $P(C_6F_5)_3$, only adduct $H_3N \rightarrow B(C_6F_5)_3$ and a new polymorph of $C_6F_5B(OH)_2$ were isolated and identified by X-ray diffraction (XRD). A molecular struc-

ture of **2a** was confirmed by XRD, and the π -stacked orientation of one of phenyl groups and heterocyclic moiety was observed. This structure is in general agreement with that calculated at the RI-MP2 level of theory, as well as at three different levels of DFT theory with the PBE and B3LYP functionals. Mild thermolysis of **2a** in a dilute decane solution gave persistent 5,7-difluoro-1,2,3-benzodithiazolyl (**3a**) identified by EPR in combination with DFT calculations. © 2014 Wiley Periodicals, Inc. *Heteroatom Chem.* 26:42–50, 2015; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21209

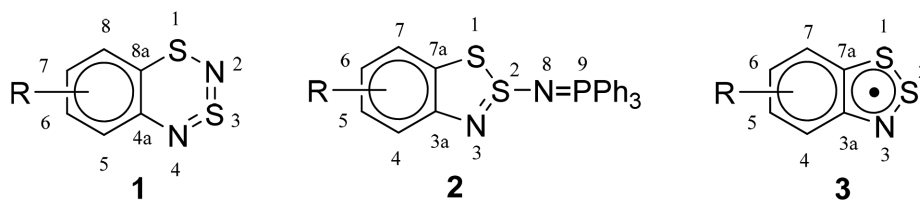
INTRODUCTION

1,3,2,4-Benzodithiadiazines (**1**, Chart 1) represent a relatively rare class of compounds possessing formal features of antiaromaticity in combination with moderate thermal stability. Their heteroatom reactivity is of obvious fundamental interest [1]. Particularly, it was found that 1,3,2,4-benzodithiadiazine and its derivatives, including low- and high-fluorinated ones (as well as 1-Se congener of trifluoro derivative) react with PPh_3

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Contract grant sponsor: Ministry of Education and Science of the Russian Federation (project of Joint Laboratories of Siberian Branch of the Russian Academy of Sciences and National Research Universities).

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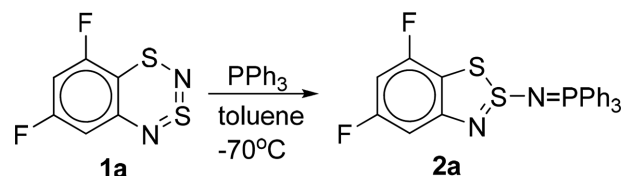
2, R = 5,7-F₂ (a), 4,5,6,7-H₄ (b), 4,5,6,7-F₄ (c), 5,6-F₂ (d), 4,5,7-F₃ (e)

CHART 1 Chemical structures and atom numbering of 1,3,2,4-benzodithiadiazines (**1**), 1,2,3-benzodithiazol-2-yl iminophosphoranes (**2**), and 1,2,3-benzodithiazolyls (**3**).

(Ph = C₆H₅) to give chiral 1,2,3-benzodithiazol-2-yl iminophosphoranes (**2**, Chart 1) inaccessible by other approaches including classical Kirsanov and Staudinger reactions [2]. The exact mechanism of this seemingly soft-EI-soft-Nu orbitally controlled reaction is unclear. Formally, 1,3,2,4-benzodithiadiazines act in this reaction as they are isomeric singlet nitrenes (observed in a cryogenic matrix as a product of their photochemical rearrangement [1, 3]), which iminate oxidatively the P atom of the phosphine. In the crystalline state, compounds **2** reveal interesting structural feature as one of Ph groups and the hetero ring are always face-to-face oriented (π -stacked) with interplanar separation being shortened as compared with the sum of corresponding van der Waals radii [1, 2]. The nature of this is not entirely clear. In solution, compounds **2** easily form corresponding 1,2,3-benzodithiazolyls (Herz radicals; **3**; Chart 1) [4], candidate-building blocks for magnetically active and/or conductive materials [5], covering derivatives inaccessible in other ways (e.g., fluorinated derivatives) [2, 5]. This approach to Herz radicals can be considered as the mildest one.

In the present work, we report on new data on the interaction between compounds **1** and PPh₃ as well as on its attempted extension to other PR₃ reagents (R = C₆F₅ (Ph_F), OPh) with different nucleophilicities. The latter can be comparatively estimated through (n_p)⁻¹ ionization energy, which is 7.80 and 9.18 eV for PPh₃ and P(Ph_F)₃, respectively, in HeI PES spectra, and 7.83 and 8.60 eV for PPh₃ and P(OPh)₃, respectively, measured by electron impact ionization [6].

With PPh₃, a new iminophosphorane **2a** was obtained, structurally characterized by XRD and converted into a new 1,2,3-benzodithiazolyl radical **3a** identified by EPR. From a slow reaction with P(OPh)₃, only S=P(OPh)₃ and O=P(OPh)₃ were identified, whereas P(Ph_F)₃ was found to catalyze hydrolysis of **1b** affording 2-amino-*N*-sulfinylbenzenesulfenamide **4**. The interaction of



SCHEME 1

1c with electrophilic B(Ph_F)₃ instead of nucleophilic P(Ph_F)₃ resulted in a complex mixture, whose workup gave an adduct H₃N→B(Ph_F)₃ and a new polymorph of C₆F₅B(OH)₂ identified by XRD. The RI-MP2 and DFT calculations on **1b** qualitatively reproduced its conformation observed in the crystal [2a].

RESULTS AND DISCUSSION

It was found that at -70°C and in toluene solution 6,8-difluoro-1,3,2,4-benzodithiadiazine (**1a**) interacts with PPh₃ to give a new iminophosphorane **2a** (Scheme 1) in the isolated yield of 37%. This is almost two times higher than the yield of its isomer **2d** (Chart 1) synthesized under identical conditions [2].

The structure of **2a** was confirmed by XRD, and face-to-face orientation of a Ph group and the heterocycle was observed (Fig. 1; discussion is given below).

With the archetypal compound **1b**, it was also found that the interaction between PPh₃ and compounds **1** is solvent dependent and concentration independent. With toluene as the solvent, high dilution of the reaction mixture (obtained at -70°C by simultaneous addition of solutions of 1 mmol of **1b** and PPh₃ in 5 mL of toluene to 30 mL of the same solvent during 1 h) did not improve the yield of a target product **2b** reported earlier (16% [2b]). Performed in diethyl ether or dichloromethane instead of toluene, the interaction under discussion did not give product **2b**; instead, unidentified tar was obtained.

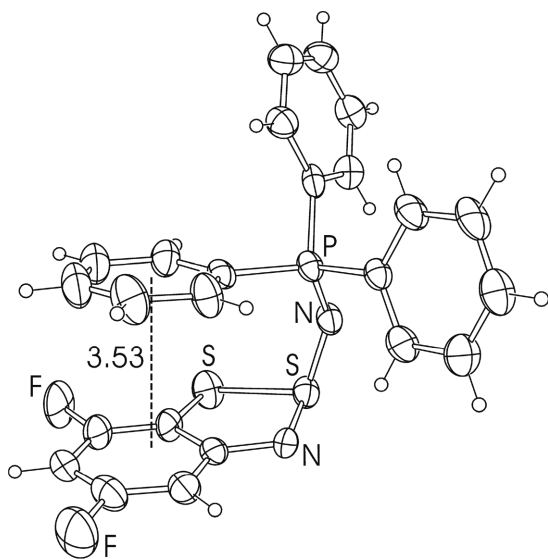
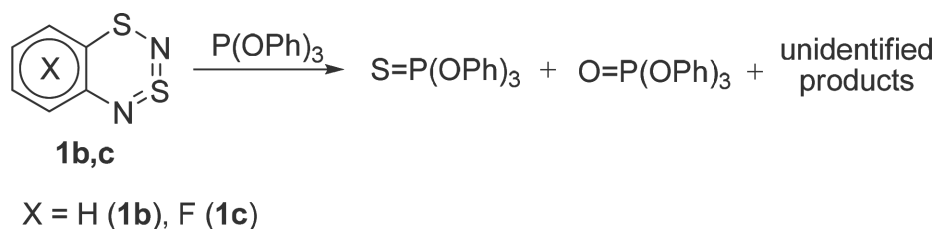


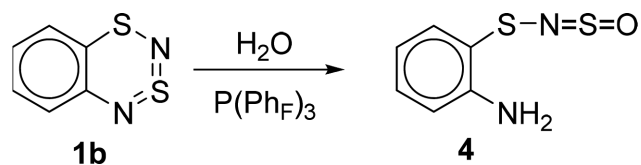
FIGURE 1 XRD structure of **2a** (displacement ellipsoids at 30%).

Other PR_3 compounds tried ($\text{R} = \text{OPh}$, Ph_F) revealed different heteroatom reactivity. Reactions required higher temperatures but even at 20°C P(OPh)_3 interacted with both hydrocarbon **1b** and fluorocarbon **1c** derivatives very slowly to give after several days complex reaction mixtures in which only $\text{X}=\text{P(OPh)}_3$ ($\text{X} = \text{S}$, O , in proportion 1:1 and 1:2.3, respectively) were identified by ^{13}C and ^{31}P NMR and GC-MS techniques (Scheme 2). In the case of $\text{X} = \text{S}$, initial compounds **1** were obviously the source of sulfur (desulfurization of sulfur–nitrogen rings, cages, and chains by PR_3 compounds is well known [1, 2c]), whereas with $\text{X} = \text{O}$ a source of oxygen is not entirely clear. The experiments were performed under argon, but their duration was 12–15 days; and atmospheric oxygen might enter the reaction systems to oxidize P(OPh)_3 into $\text{O}=\text{P(OPh)}_3$.

The interaction of compounds **1** with the phosphorus reagents is thought to begin with neutralization of Lewis acid (compound **1**) by Lewis base (phosphine or phosphite). The yields of compounds **2** are higher for starting **1** with higher calculated electron affinity and experimental reduction poten-



SCHEME 2



SCHEME 3

tial [2a,7] whose values can be used for comparative estimation of their Lewis acidity. Reduced Lewis basicity of P(OPh)_3 leads to zero yield of the imination product.

In the toluene solution of **1b**, $\text{P(Ph}_F)_3$ remained unchanged even under reflux (^{19}F NMR). It is known that compounds **1** are stable under these conditions [8] and their decomposition with formation of radicals **3** requires higher temperatures [2a,b,9]. After evaporation of the reaction mixture and dissolving the residue in CDCl_3 without protection from atmospheric moisture, ^1H NMR spectrum of the reaction solution revealed, however, the presence of 2-amino-*N*-sulfinylbenzenesulfenamide (**4**, Scheme 3) together with starting **1b**. Previously, this product was obtained by 1:1 addition of atmospheric H_2O to **1b** catalyzed by SbPh_3 [2a] (cf. [10]). Taking into account that compound **1b** itself does not add H_2O at the same conditions, one can conclude that $\text{P(Ph}_F)_3$ also very effectively catalyses addition of atmospheric water to **1b**, and that Lewis bases catalytic contribution to heteroatom reactivity of compounds **1** is worth of further investigation. Seemingly, this result gives a new example of catalytic action of frustrated Lewis pair [11].

Overall, the data obtained lead to conclusion that the scope of interaction between compounds **1** and PR_3 derivatives affording iminophosphoranes **2** is limited because only PPh_3 gives the target compounds whereas other PR_3 tried ($\text{R} = \text{OPh}$, Ph_F) do not.

In experiments with compound **1c** and electrophilic $\text{B(Ph}_F)_3$ instead of nucleophilic $\text{P(Ph}_F)_3$, a complex mixture of products was observed by ^{19}F NMR. The products were extremely moisture sensitive and decomposed fast in contact with

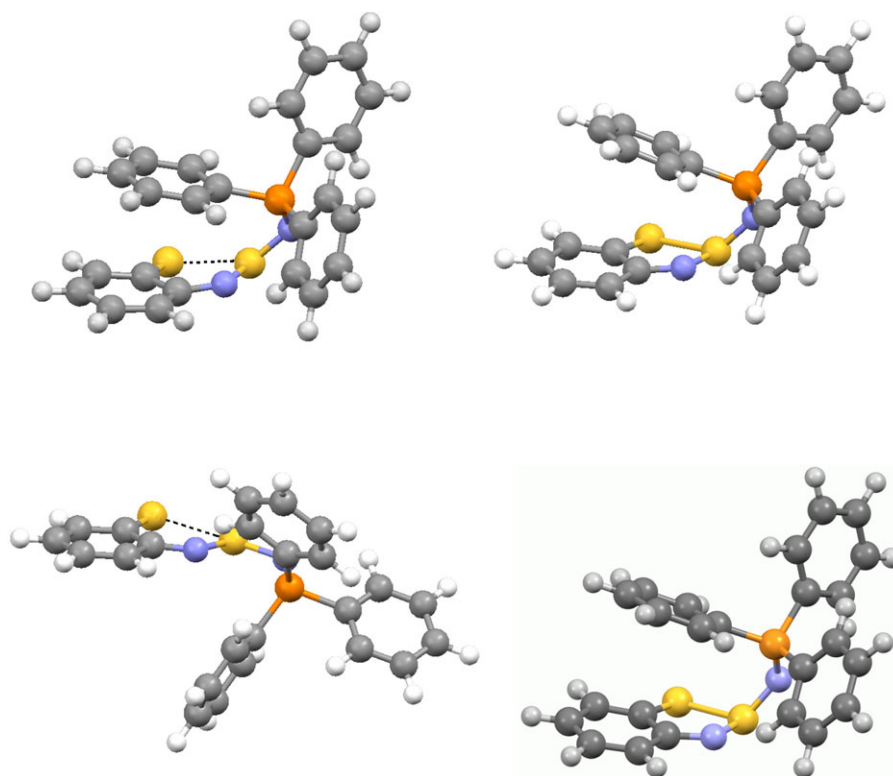


FIGURE 2 Molecular conformation of **2b** optimized at the RI-MP2/L1 (top left), PBE/3z (top right), B3LYP/6-311G (bottom left) and PBE/L22 (bottom right) levels of theory.

air during workup of the reaction mixture. Only adduct $\text{H}_3\text{N}\rightarrow\text{B}(\text{Ph}_F)_3$ and a new polymorph of $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ were isolated and identified by XRD (in the Supporting Information). One can think that these compounds came from air-moisture hydrolysis of the primary reaction products. It should be noted that little is known about reactivity of chalcogen-nitrogen heterocycles related to compounds **1** toward BR_3 derivatives. In this context, only molecular complexes between BR_3 and 2,1,3-benzochalcogenadiazoles can be mentioned [12].

The XRD structure of compound **2a** (Fig. 1) gives another example of face-to-face orientation of one of the Ph groups and the heterocyclic moiety typical of compounds **2**. For previously studied derivatives, it was observed that the corresponding interplanar separation decreases with an increase in the number of fluorine atoms as 3.52 (**2b**), 3.49 (**2d**), 3.43 (**2e**), and 3.39 (**2c**) Å [2] (for chemical structures, see Chart 1). Compound **2a**, however, does not fit into this sequence since the observed interplanar separation of 3.53 Å not only exceeds that for isomeric **2d** but also is the biggest separation found so far. In the crystal, weak hydrogen bonds $\text{C}-\text{H}\cdots\text{N}$ ($\text{H}\cdots\text{N}$ 2.55 Å, $\text{C}-\text{H}\cdots\text{N}$ 156°) lead to formation of one-dimensional chains. In addition to the

$\text{H}\cdots\text{N}$ interaction, the $\text{C}-\text{F}\cdots\pi$ interaction of the fluorine atom of the $\text{C}-\text{F}$ bond of one molecule with a fluorinated benzene ring of another is observed; the atom-to-plane distance is 3.44 Å.

It remains unclear whether the conformation observed is a result of intramolecular interactions (including π -stacking interactions of the arene-(poly)fluoroarene type, [2a and references therein]), or of intermolecular ones (packing forces of the crystal lattice), or of their interplay. To investigate the geometry of free molecules of **2**, quantum chemical calculations of the archetypal compound **2b** were performed. Previously DFT methods were successfully used for the calculation of structure and properties of **1**, **3**, 1,2,3-benzodichalcogenazolium cations and some other related compounds [1, 3, 4a,c,8d-f,9, 13, 14]. The MP2 method also gave satisfactory results for 1,2,3-benzodithiazolium cation but not good ones for the compounds **1** [14].

In this work, the RI-MP2 and DFT optimization of molecular geometry of **2b** at four different levels of theory gives molecular conformations (Fig. 2) whose shape is similar to that observed by XRD (Fig. 1). At the same time, experimental and theoretical molecular geometries differ in two important aspects: (1) the S—S bond in the XRD structures (**2b**,

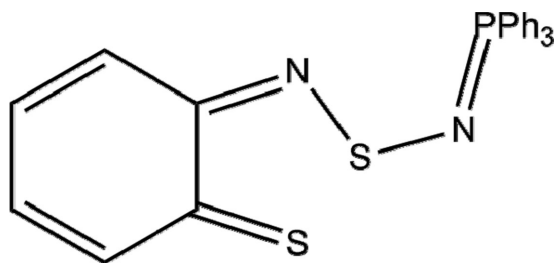
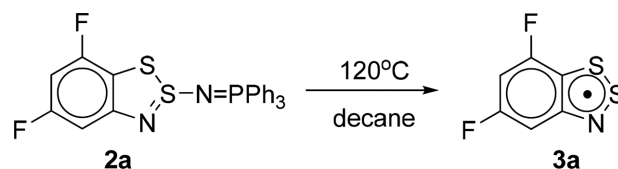


CHART 2 Structure of **2b** corresponding to the B3LYP/6-311G calculations.

2.17 [2b]; **2a**, 2.18 Å) is markedly shorter than in the calculated structures (RI-MP2, 2.57; PBE/3z, 2.46; PBE/L22 2.32; B3LYP, 2.90 Å) where it is conformation dependent (in the Supporting Information) and (2) the intercentroid separation in the XRD structures of 3.56 Å [2a] is significantly smaller than in the DFT-calculated ones (PBE/3z, 4.18; PBE/L22, 4.02; B3LYP, 5.52 Å); at the same time, RI-MP2 results (3.48 Å) agree well with the experiment (for detailed results of the calculations, see the Supporting Information). Some other conformations of **2b** were also optimized by the same methods. In many cases, they were less stable than the discussed conformations only by a few kcal mol⁻¹ and revealed shorter S—S bonds (down to 2.18 Å; see the Supporting Information for details).

The B3LYP/6-311G distance of 2.90 Å is too long for the S—S bond whose typical length is 2.02–2.08 Å [15]. In this respect, the calculated structure is closer to the structure shown in Chart 2 than to the structure represented in Chart 1.

Overall, one may think that the experimental molecular conformation under discussion is an interplay of inter- and intramolecular interactions. The calculations also reveal high flexibility of the compound **2b**, which is worth of further investigation (for instance, by methods of variable-temperature NMR).



SCHEME 4

Upon moderate heating in dilute hydrocarbon solutions or, in some cases, just dissolving in chloroform at ambient temperature, compounds **2** transform into radicals **3** [1, 5, 9]. Both approaches were applied to **2a**. Under heating of **2a** in decane solution at 120°C, an EPR spectrum corresponding to 5,7-difluoro-1,2,3-benzodithiazolyl (**3a**) was acquired (Scheme 4 and Fig. 3). At the same time, the chloroform solution of **2a** was EPR-silent over a 2-week period of observation. Previously, the formation of radicals **3** under the latter conditions was observed by EPR in the case of **2b–d** but not of **2e** [2a,b,9]. Seemingly, the different ratios of rate constants of radicals' generation and decay may be a reason of this situation.

The electrochemical reduction of **2c** was also tried in this work. It was suggested that its radical anion will decompose into persistent 4,5,6,7-tetrafluoro-1,2,3-benzodithiazolyl [9] and anion Ph₃P=N⁻. The reduction peak at -0.96 V was expectedly irreversible, but the reaction system was EPR-silent.

EXPERIMENTAL

General

¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were measured with a Bruker AV-300 machine at frequencies of 300.13, 75.47, 282.40, and 121.49 MHz, respectively, for CDCl₃ solutions, except for C₆D₆ solutions of products from experiments with P(OPh)₃ and toluene-C₆D₆ solutions of products from

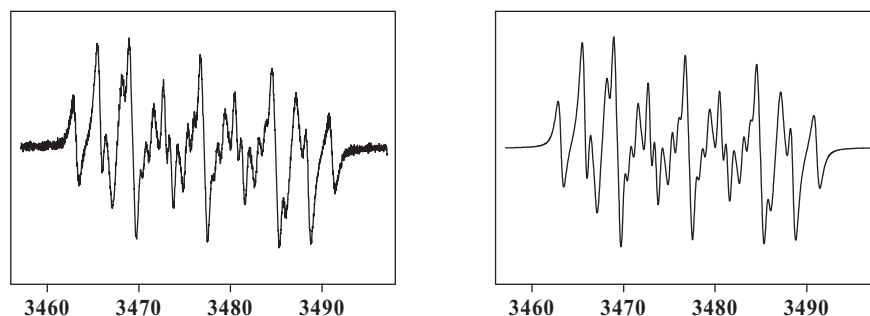


FIGURE 3 Experimental (left) and simulated (right) EPR spectrum of **3a**. The experimental (B3LYP/6-31G calculated) hfc constants (G): a_N^3 7.8 (8.5), a_H^4 2.6 (3.6), a_H^6 3.4 (4.1), a_F^5 2.6 (3.7), a_F^7 3.8 (4.6).

experiments with $B(\text{Ph}_F)_3$. The standards were TMS (^1H , ^{13}C), C_6F_6 (^{19}F ; $\delta = -162.9$ ppm with respect to CFCl_3), and 85% H_3PO_4 (^{31}P).

High-resolution MS spectra (IE, 70 eV) were obtained using a Thermo DFS mass-spectrometer. GC-MS determinations were performed with a Hewlett-Packard G1800A GDC instruments, and with an Agilent Technologies apparatus comprising a gas chromatograph Agilent 6890N and a chromatography-mass-spectrometry system Agilent 5973N.

Compounds **1** [6], PR_3 ($\text{R} = \text{OC}_6\text{H}_5$ [16], C_6F_5 [17]), and $B(\text{Ph}_F)_3$ [18] were prepared as described before; other chemicals were commercially available. Solvents were dried with common drying agents.

EPR Spectroscopy

EPR spectra were acquired using a Bruker ESP-300 spectrometer (modulation frequency, 100 kHz; modulation amplitude, 0.05 G; MW power, 265 mW). Simulations of the experimental EPR spectra were performed with the *Winsim 2002* program [19]. The accuracy of the hyperfine coupling (hfc) constants was 1×10^{-2} G.

X-Ray Diffraction

The XRD data were collected with a Bruker Kappa Apex II CCD diffractometer using ϕ , ω scans of narrow (0.5°) frames with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite monochromator at $T = 240$ (2) K. The structures were solved by direct methods and refined by full-matrix least-squares method against all F^2 in anisotropic approximation (isotropic for H atoms in compound $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$) using the *SHELX-97* programs set [20]. The H atoms positions were calculated with the riding model for **2a**, and the H atom positions for $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ were located from the difference Fourier map. Absorption corrections were applied empirically using *SADABS* programs [21]. Compound **2a**: monoclinic, space group *Cc*, $a = 9.788(2)$, $b = 15.898(3)$, $c = 14.307(3) \text{ \AA}$, $\beta = 92.432(7)^\circ$, $V = 2224.3$ (8) \AA^3 , $Z = 4$, $\text{C}_{24}\text{H}_{17}\text{F}_2\text{N}_2\text{PS}_2$, $D_c = 1.393 \text{ g cm}^{-3}$, $\mu = 0.342 \text{ mm}^{-1}$, $F(0\ 0\ 0) = 960$, crystal size $0.04 \times 0.04 \times 0.04 \text{ mm}^3$, independent reflections 2872, $wR_2 = 0.1424$, $S = 1.05$ for all reflections ($R = 0.0545$ for 2051 $F > 4\sigma$). Compound $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$: monoclinic, space group *P2*₁, $a = 7.455(1)$, $b = 5.0070(7)$, $c = 10.055$ (2) \AA , $\beta = 96.784(6)^\circ$, $V = 372.7(1) \text{ \AA}^3$, $Z = 2$, $\text{C}_6\text{H}_2\text{F}_5\text{BO}_2$, $D_c = 1.888 \text{ g cm}^{-3}$, $\mu = 0.214 \text{ mm}^{-1}$, $F(0\ 0\ 0) = 208$, crystal size $0.04 \times 0.04 \times 0.9 \text{ mm}^3$, independent reflec-

tions 1167, $wR_2 = 0.1117$, $S = 1.10$ for all reflections ($R = 0.0396$ for 1075 $F > 4\sigma$). The obtained crystal structures were analyzed for short contacts between nonbonded atoms using the *PLATON* program [22].

Quantum Chemical Calculations

Theoretical hfc constants of radical **3a** were obtained at the B3LYP/6-31G level of theory with the *GAMESS* program [23a]. Molecular conformations of compounds **2** were calculated with the *GAMESS* (B3LYP) and *PRIRODA* (RI-MP2, PBE) [23b,c]. The L1 (an analog of cc-pVDZ) [23d], L22 (cc-pCVTZ), and 3z basis sets were used as implemented in the *PRIRODA* program.

Cyclic Voltammetry of Iminophosphorane **2c**

The CV measurements on compound **2c** (10^{-3} M solution in dry MeCN) were performed at 298 K in an argon atmosphere with a PG 310 USB potentiostat (HEKA Elektronik). A stationary platinum electrode ($S = 0.08 \text{ cm}^2$) was used. A supporting electrolyte was 0.1 M Et_4NClO_4 . The peak potential was quoted with reference to a saturated calomel electrode (SCE).

Syntheses

Compound 2a. At -70°C and under argon, a solution of 0.284 g (1.1 mmol) of PPh_3 in 5 mL of toluene was added dropwise to a stirred solution of 0.221 g (1.1 mmol) of **1a** in 5 mL of toluene over a period of 1 h. The reaction mixture was slowly warmed up to 20°C and stirred for additional 1.5 h. Then 15 mL of hexane was layered over the reaction mixture to produce a two-layered system. The system was kept at ambient temperature until mutual diffusion of solvents ceased. The solution and tarry residue were separated, and the solution was layered again with 15 mL of hexane. Compound **2a** was obtained in the form of dark-red crystals (0.187 g, 37%) suitable to XRD, m p $126\text{--}127^\circ\text{C}$. NMR, δ : ^1H : 7.62–7.53 (9H, broad unresolved signal), 7.45–7.39 (6H, broad unresolved signal), 6.35 (1H, d), 6.05 (1H, d); ^{13}C : 161.8, 160.4, 156.0, 132.8 (two overlapping signals), 128.6, 126.4, 107.9, 97.8, 92.4; ^{19}F : 58.1, 44.3; ^{31}P : 19.7. MS M^+ , m/z , measured (calculated for $\text{C}_{24}\text{H}_{17}\text{F}_2\text{N}_2\text{PS}_2$): 466.0530 (466.0533). Found (calculated), C 61.87 (61.79), H 3.60 (3.67), N 5.92 (6.00), F 8.17 (8.14), P 6.58 (6.64), S 13.90 (13.75).

Reaction of **1b** and **1c** with $P(\text{O}Ph)_3$

At -70°C and under argon, a solution of 0.310 g (1.0 mmol) of $P(\text{O}Ph)_3$ in 5 mL of toluene was added

dropwise to a stirred solution of 1.0 mmol of **1b** or **1c** in 5 mL of toluene over a period of 1 h. The reaction mixture was slowly warmed up to 20°C and kept further at this temperature. The ^{31}P NMR spectra were measured periodically, indicating the disappearance of the signal of $\text{P}(\text{OPh})_3$ ($\delta = 128$ ppm) after 12 days (**1b**) or 15 days (**1c**). The main signals in the ^{31}P NMR spectra of the reaction mixtures belong to $\text{O}=\text{P}(\text{OPh})_3$ (−17 ppm) and $\text{S}=\text{P}(\text{OPh})_3$ (54 ppm) in proportion 1:2.3 (**1b**) or 1:1 (**1c**). The presence of $\text{O}=\text{P}(\text{OPh})_3$ and $\text{S}=\text{P}(\text{OPh})_3$ in the reaction mixtures was also confirmed by ^{13}C NMR. According to ^1H or ^{19}F NMR spectra, the mixtures also contained starting **1b** or **1c**. The solvent evaporation under reduced pressure gave tarry products from which unconsumed compounds **1** were recovered in the yield of 10–15% by sublimation at 50°C/1 Torr. GC-MS analysis of the residue revealed the same ratio of $\text{O}=\text{P}(\text{OPh})_3$ and $\text{S}=\text{P}(\text{OPh})_3$ as indicated above.

Transformation of 1b in the Presence of $\text{P}(\text{C}_6\text{F}_5)_3$

Under a CaCl_2 tube, a solution of 0.445 g (0.8 mmol) of $\text{P}(\text{C}_6\text{F}_5)_3$ in 5 mL of toluene was added to a stirred solution of 0.140 g (0.8 mmol) of **1b** in 5 mL of toluene, and the reaction mixture was refluxed for 2 h. Upon cooling to 20°C, ^{19}F NMR spectrum was measured to reveal unchanged $\text{P}(\text{C}_6\text{F}_5)_3$. The solvent was distilled off, and the residue was dissolved in CDCl_3 . Two last operations were performed without protection from atmospheric moisture. According to the ^1H NMR, CDCl_3 solution contained a mixture of starting **1b** and a water-addition product **4** [**2a**] in a 42:58 ratio.

Generation of Radical 3a

Under argon, a solution of 7 mg (1.5×10^{-5} mol) of **2a** in 1 mL of degassed decane was kept at 120°C for 40 min, cooled to 20°C, and its EPR spectrum was measured to reveal radical **3a**.

Interaction of 1c with $\text{B}(\text{C}_6\text{F}_5)_3$ and Isolation of a New Polymorph of $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$

At −70°C and under argon, a solution of 0.399 g (0.8 mmol) of $\text{B}(\text{C}_6\text{F}_5)_3$ in 6 mL of toluene was added dropwise to a stirred solution of 0.187 g (0.8 mmol) of **1c** in 5 mL of toluene over a period of 80 min during which the solution was turning dark-brown. Upon warming to 20°C, ^{19}F NMR spectrum was measured to reveal a complex mixture of unassigned signals. A part of the solution was evaporated, and the residue was crystallized twice from hexane without protection from atmospheric moisture. An adduct

$\text{H}_3\text{N} \rightarrow \text{B}(\text{Ph}_\text{F})_3$ [**24**] was obtained in the form of dark-purple crystals suitable to XRD and identified by the unit cell parameters. Another part of the reaction solution was evaporated and left at ambient temperature for 1 week. White needles of $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ appeared on the walls of the vessel that were suitable for XRD.

CONCLUSIONS

The general character of reaction between 1,3,2,4-benzodithiadiazines and PPh_3 affording chiral 1,2,3-benzodithiazol-2-yl iminophosphoranes inaccessible by other ways was confirmed with another example, as well as ability of the iminophosphoranes to produce 1,2,3-benzodithiazolyls (Herz radicals) under mild conditions. However, it was found that this reaction cannot be transferred from PPh_3 to $\text{P}(\text{OPh})_3$ and $\text{P}(\text{Ph}_\text{F})_3$. The first one produces only unidentified tar together with $\text{S}=\text{P}(\text{OPh})_3$ and $\text{O}=\text{P}(\text{OPh})_3$ as a result of a slow reaction. The second one does not react at all under studied conditions but, similar to SbPh_3 , effectively catalyzes water addition to 1,3,2,4-benzodithiadiazines. The lower nucleophilicity of $\text{P}(\text{OPh})_3$ and $\text{P}(\text{Ph}_\text{F})_3$ as compared with PPh_3 seems to be the cause of these findings. Thus, more reactive P-nucleophiles like donor-substituted triarylphosphines, alkyl- and aminophosphines are thought to be promising for further development of this method for the synthesis of iminophosphoranes.

The XRD structure of **2a** gave another example of face-to-face orientation of one of the Ph groups and the heterocyclic moiety typical of the 1,2,3-benzodithiazol-2-yl iminophosphoranes. This special structure is in a general agreement with the results of both post-HF and DFT calculations. Overall, one may think that the XRD molecular conformation of the 1,2,3-benzodithiazol-2-yl iminophosphoranes is an interplay of inter- and intramolecular interactions. The former are packing forces of the crystal lattice, whereas the latter in the case of fluorocarbon derivatives may involve π -stacking interactions of the arene-(poly)fluoroarene type.

In experiments with **1c** and electrophilic $\text{B}(\text{Ph}_\text{F})_3$ instead of nucleophilic PR_3 reagents, a complex mixture of products was observed, with only adduct $\text{H}_3\text{N} \rightarrow \text{B}(\text{Ph}_\text{F})_3$ and a new polymorph of $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ being isolated and identified by XRD.

ACKNOWLEDGMENTS

The authors are grateful to Prof. Dr. Vadim V. Bardin for generous gift of $\text{B}(\text{C}_6\text{F}_5)_3$ and helpful discussions, to Dr. Nadezhda V. Vasileva for the electrochemical

experiments, to Dr. Alexander M. Genaev for PBE/L22 calculations, and to Dr. Arkady G. Makarov for help in some preparations. They also thank the Collective Chemical Service Center of Siberian Branch of the Russian Academy of Sciences for instrumental facilities.

SUPPLEMENTARY DATA

CCDC 940262 and 940263 contain the supplementary crystallographic data for **2a** and $C_6F_5B(OH)_2$, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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