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C-Phosphorylation of 1,2,4-Triazoles with Phosphorus(III) Halides. Synthesis of 4,5-Dihydrobenzo[*e*][1,2,4]Triazolo[5,1-*c*][1,4,2]Diazaphosphinine Derivatives

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ABSTRACT: *Phosphorylation of 4- and 1-substituted 1,2,4-triazoles with PCl_3, $PhPCl_2$, Ph_2PCl, and $(Et_2N)_2PCl$ was carried out. A novel phosphorus-containing condensed heterocyclic system (***18, 23***) was constructed by the reactions of 2-(1*H*-1,2,4-triazol-1-yl)-1-(4-chlorophenylcarboxamido)-5-trifluoromethylbenzene with PBr_3 and $PhPBr_2$. Treatment of the bromophosphonite* **18** *with an excess of morpholine in the presence of sulfur resulted in a diazaphosphinine ring opening and provided functionalized 1*H*-1,2,4-triazol-5-ylphosphonic acid derivatives* **21** *and* **22**. © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:146–152, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10010

INTRODUCTION

Recently, the 1,3-azoles having two heteroatoms were shown to react readily with phosphorus(III) halides to yield the corresponding products of *meso*-phosphorylation. The detailed studies on the phosphorylation of imidazoles and benzimidazoles [1], thiazoles and benzothiazoles [2] have been reported.

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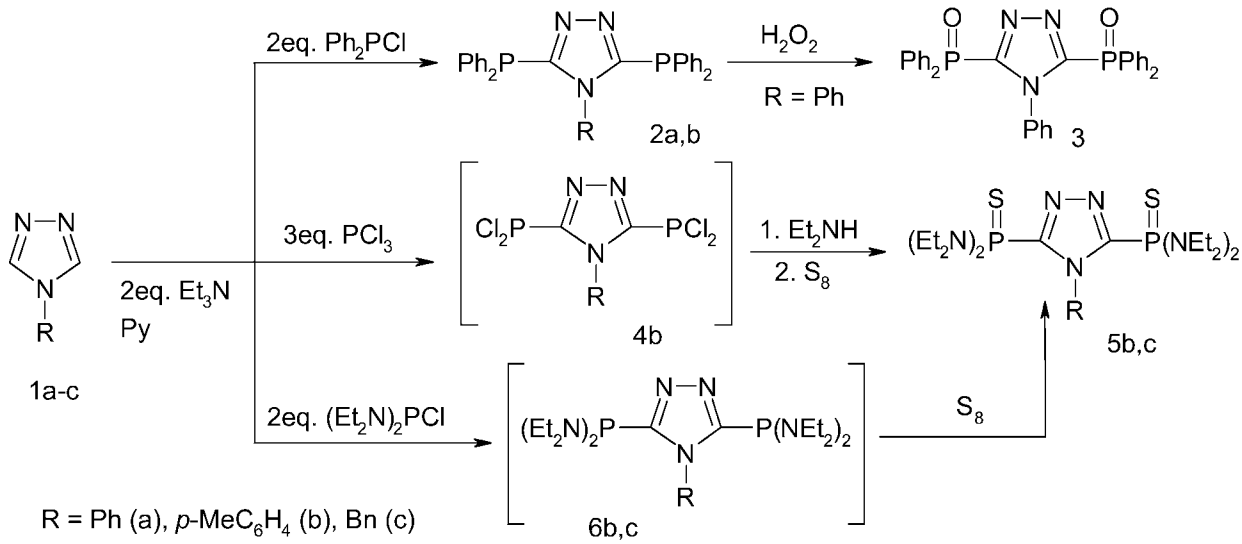
As an extension of our research on the direct *C*-phosphorylation of 1,3-azoles with phosphorus(III) halides, we studied the 1,2,4-triazole ring system in this reaction. A general approach to *C*-phosphorylated heterocycles via their lithiated derivatives has been found suitable for the syntheses of *C*-phosphorylated 1*H*- as well as 4*H*-1,2,4-triazoles [3,4]. However, owing to the low stability of the intermediate organometallic species, only moderate yields of the final products were obtained in some cases. As demonstrated in our preliminary communication [5], introduction of a nitrogen atom into the imidazole ring facilitates phosphorylation. Herein, we report on the extended study of the phosphorylation of both 4- and 1-substituted 1,2,4-triazoles along with the phosphorylation of the functionalized triazole **17**, which resulted in the construction of a novel phosphorus-containing condensed heterocyclic system.

RESULTS AND DISCUSSION

The 4-substituted 1,2,4-triazoles have two potential sites (in *meso*-positions) for the attack by a phosphorylating agent. An attempt to introduce one Ph_2P moiety into **1a,b** by the treatment with equimolar quantities of Ph_2PCl resulted in nonseparable mixtures of mono- and bis-phosphorylated products. The latter (**2a,b**) were, however, sole products when two equivalents of the phosphorylating agent were



SCHEME 1

employed (Scheme 1, Table 1). The phosphine **2a** was converted into the phosphorus(V) derivative **3** upon treatment with hydrogen peroxide. Similarly, PCl_3 reacts with **1b** to produce the single product bis-dichlorophosphinotriazole (**4b**) when the reagents are taken in a 2:1 ratio. **4b**, without isolation, was subsequently treated with diethylamine and sulfur to furnish **5b**.

TABLE 1 Experimental Data of the Compounds Prepared

Compound	*Yield (%)*	*mp/bp (°C)*	*Formula*	$\delta^{31}P$ [a] *(Solvent)*	*Found (%)*	
					N	*P*
2a	59	153–155 (benzene)	$C_{32}H_{25}N_3P_2$	−31.6 (CH_2Cl_2)	8.09 (8.18)[b]	12.14 (12.06)[b]
2b	57	133–144 (EtOAc)	$C_{33}H_{27}N_3P_2$	−31.5 ($CHCl_3$)	8.01 (7.97)	11.63 (11.74)
3	81	218	$C_{33}H_{27}N_3O_2P_2$	15.0 (CH_2Cl_2)	7.56 (7.51)	11.10 (11.07)
5b	35–55	111–112 (hexane)	$C_{25}H_{47}N_7P_2S_2$	56.0 ($CHCl_3$)	17.06 (17.15)	10.90 (10.83)
5c	57	110–111 (hexane)	$C_{25}H_{47}N_7P_2S_2$	58.2 (toluene)	17.11 (17.15)	10.94 (10.83)
8	60	139–140 (EtOH)	$C_{21}H_{18}N_3P$	−32.8 (pyridine)	12.19 (12.24)	8.95 (9.02)
10	68	89–90 (EtOAc)	$C_{15}H_{14}N_3P$	−30.8 ($CHCl_3$)	15.61 (15.72)	11.64 (11.59)
13	51	79–81(0.04)[c]	$C_7H_{16}N_5P$	76.5 (benzene)	34.90 (34.81)	15.44 (15.39)
14	26	125–127(0.06)[c]	$C_8H_{14}N_7P$	27.7 (benzene)	41.08 (40.99)	12.86 (12.95)
19a	26	225–226 (benzene/heptane)	$C_{20}H_{16}ClF_3N_5O_2PS$	42.8 ($CDCl_3$)	14.37 (13.63)	5.78 (6.03)
19b	51	215–216 (toluene/heptane)	$C_{22}H_{13}ClF_3N_4OPS$	40.1 (DMSO)	11.13 (11.10)	6.00 (6.14)
21	61	183–184 (toluene/heptane)	$C_{24}H_{25}ClF_3N_6O_3PS$	53.4 ($CDCl_3$)	14.01 (13.98)	5.32 (5.15)
22	93	151–152 (EtOH/H_2O 1:1)	$C_{17}H_{22}F_3N_6O_2PS$	53.6 ($CDCl_3$)	18.19 (18.17)	6.61 (6.70)

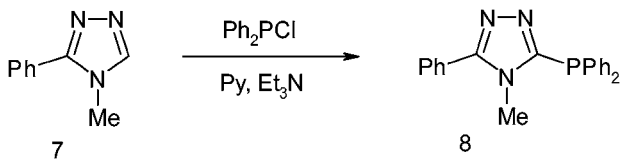
[a]Solvent used is given in parentheses.
[b]Values within parentheses in these columns indicate percent calculated values.
[c]mm Hg.

The high reactivity of 1,2,4-triazole allowed us to synthesize the phosphamides **5b,c**, even using a phosphorylating agent of such low reactivity as tetraethyldiamidochlorophosphite. A strong effect of the nature of an *N*-substituent on the substrate reactivity was observed in this case. 4-Benzyl-4*H*-1,2,4-triazole (**1c**) was allowed to react with 2 equivalents of $(Et_2N)_2PCl$ to yield the phosphamide **6c** in 3 days. On the other hand the same reaction of **1b**, having the aryl substituent at the nitrogen, proceeds extremely slowly and is complete only in 1 year.

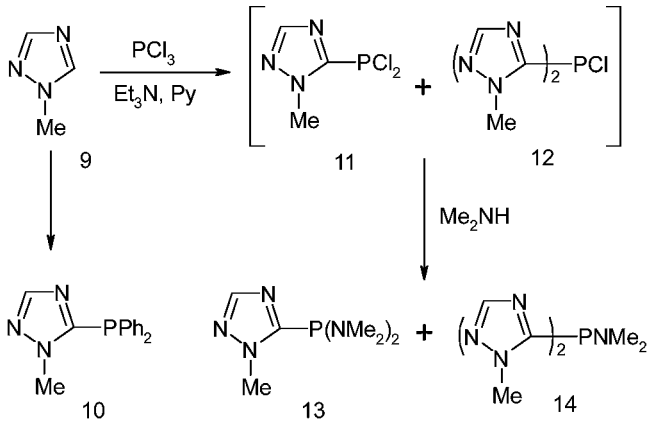
The difficulty of preparation of a monophosphorylated 4-substituted 1,2,4-triazole was resolved by blocking one of the reactive sites with an indifferent substituent, namely the phenyl group, as in the triazole **7**, which was phosphorylated with diphenylchlorophosphine to produce the phosphine **8** (Scheme 2).

1-Methyl-1*H*-1,2,4-triazole (**9**), in contrast to the *sym*-triazoles **1**, has only one potential phosphorylation site, which is located between nitrogen atoms of the pyrrole and pyridine types. The reaction of **9** with diphenylchlorophosphine yielded the phosphine **10** (Scheme 3). When PCl_3 was allowed to react with the triazole **9**, a mixture of chlorophosphines **11** and **12** was obtained. The ratio of products approaches 1:1 as the temperature of the phosphorylation is increased. The chlorophosphines **11** and **12** cannot be separated by simple distillation because of their thermal instability. Treatment of a mixture of **11** and **12** with dimethylamine afforded the corresponding mixture of phosphamides **13** and **14**, that subsequently could be separated by distillation.

Finally, we carried out phosphorylation of the functionalized triazole **17** in the manner described previously for the analogous imidazole derivative [6]. The starting amide **17** was synthesized according to Scheme 4. It was treated with PBr_3 to afford the tricyclic compound **18** (Scheme 5). Substitution of the bromine atom in **18** with morpholine, followed by sulfur addition, gave rise to the phosphorus(V) derivative **19a**. When an excess of morpholine was used in the presence of sulfur, the intermediately formed phosphamide **20** underwent a diazaphosphinine ring opening to yield the phosphorylated functionalized triazole **21**. It was found,



SCHEME 2



SCHEME 3

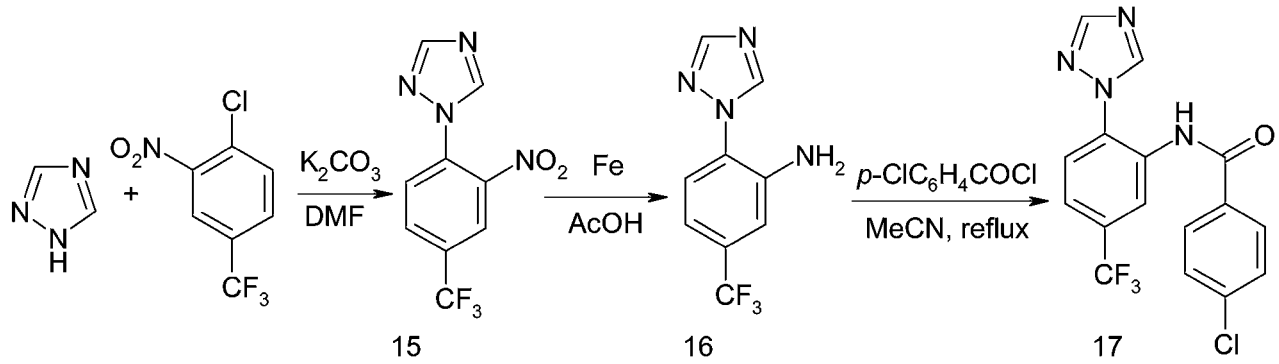
that the phosphorus moiety in **21** remained intact under the conditions of basic hydrolysis, the aniline **22** being produced. Dibromophenylphosphine was reacted with the amide **17** to produce the tricyclic **23**, which was characterized in the form of a phosphorus(V) derivative **19b**. A good correlation between ^{31}P NMR spectral data of the phosphorus compounds derived from **17** and the analogous imidazole derivatives [6] was observed. It is also worth noting that the reactivity of the herein-investigated functionalized triazole **17** is lower than that of the analogous imidazole derivative. This contrasts with the above-demonstrated high reactivity of the simple 1,2,4-triazoles. However, the observed phenomenon is plausibly due to the decreased basicity of the triazole moiety in **17**.

EXPERIMENTAL

All the manipulations with air-sensitive compounds were performed under an atmosphere of dry argon by using standard Schlenk techniques. Solvents were purified by conventional procedures. Melting points were determined with an electrothermal capillary melting point apparatus and are uncorrected. The ^{31}P, ^{1}H, ^{13}C NMR spectra were obtained on a Varian VXR-300 spectrometer (121, 300, and 75 MHz, respectively). Chemical shifts are reported relative to internal tetramethylsilane (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P).

*3,5-Bis-diphenylphosphino-4-phenyl-4H-1,2,4-triazole (***2a***) and 3,5-Bis-diphenylphosphino-4-p-tolyl-4H-1,2,4-triazole (***2b***)*

To a stirred mixture of triazole **1** (20 mmol), Et_3N (40 mmol), and pyridine (25 ml) was added Ph_2PCl (40 mmol). The reaction mixture was kept at room temperature for 24 h, then evaporated to dryness



SCHEME 4

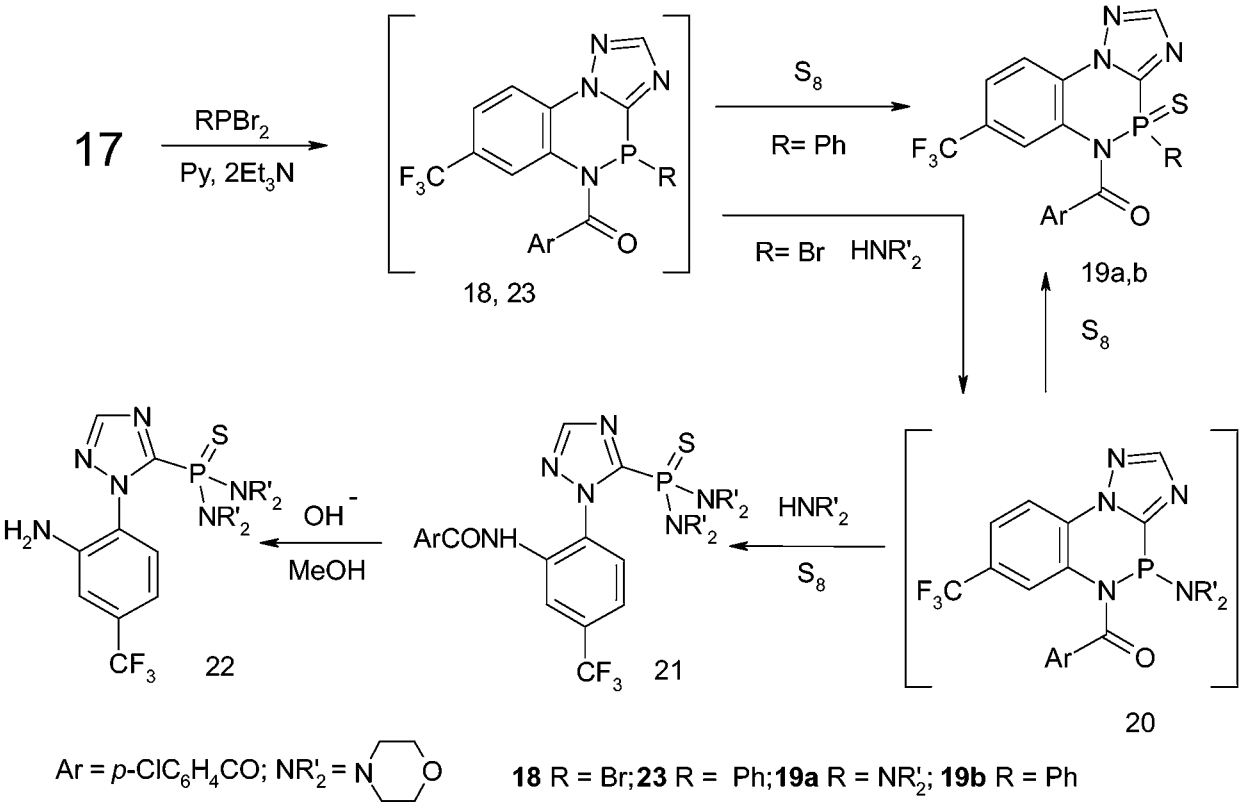
under reduced pressure. The residue was extracted with hot benzene (40 + 20 ml). The extract was evaporated to dryness under reduced pressure, and the residue was recrystallized from benzene.

2a: ^{1}H NMR ($CDCl_3$): δ (ppm) 7.49 (m, 8H, *o*-Ph_2P), 7.30 (m, 13H, *m,p*-Ph_2P + *p*-Ph-N), 7.19 (t, $J = 7.8$ Hz, 2H, *m*-Ph-N), 6.74 (d, $J = 7.7$ Hz, 2H, *o*-Ph-N). ^{13}C NMR ($CDCl_3$): δ 156.77 ppm (dd, $J = 19.5$ Hz and 2.2 Hz, C-3(5)).

2b: ^{1}H NMR (acetone-d_6): δ (ppm) 7.46 (m, 8H, *o*-Ph_2P), 7.37 (m, 12H, *m,p*-Ph_2P), 7.11 (d, $J = 8.4$ Hz, 2H, *m*-Ph-N), 6.81 (d, $J = 8.4$ Hz, 2H, *o*-Ph-N), 2.34 (s, 3H, CH_3).

*3,5-Bis-diphenylphosphinoxido-4-phenyl-4H-1,2,4-triazole (**3**)*

To a stirred solution of **2a** (10 mmol) in CH_2Cl_2 (20 ml) was added 2 M of H_2O_2 (10 ml). After 20 min, the organic layer was separated, washed with water (2 × 20 ml), dried over Na_2SO_4, and evaporated



SCHEME 5

to dryness under reduced pressure. The residue was recrystallized.

^{1}H NMR ($CDCl_3$): δ (ppm) 7.70 (m, 8H, *o*-Ph_2PO), 7.50 (m, 4H, *p*-Ph_2PO), 7.38 (m, 8H, *m*-Ph_2PO), 7.19 (t, $J = 7.7$ Hz, 1H, *p*-Ph-N), 7.01 (t, $J = 7.7$ Hz, 2H, *m*-Ph-N), 6.87 (d, $J = 7.7$ Hz, 2H, *o*-Ph-N). ^{13}C NMR ($CDCl_3$): δ 153.60 ppm (dd, $J = 20.9$ Hz and 4.7 Hz, C-3(5)).

*3,5-Bis-(tetraethyldiamidothiophosphono)-4-p-tolyl-4H-1,2,4-triazole (**5b**)*

Method A: To a stirred mixture of **1b** (10 mmol), Et_3N (20 mmol), and pyridine (10 ml) was added PCl_3 (30 mmol). After 1 h, the reaction mixture was treated with Et_2NH (0.16 mol) at 0°C and then with sulfur (30 mmol), stirred for 30 min, and evaporated under reduced pressure to dryness. The residue was extracted with benzene (30 ml). The extract was evaporated and the residue was subjected to column chromatography using hexane/EtOAc 3:1 as eluent. The product was purified by recrystallization.

Method B: To a stirred mixture of **1b** (10 mmol), Et_3N (20 mmol), and pyridine (10 ml) was added $(Et_2N)_2PCl$ (20 mmol). After 72 h, the ^{31}P NMR spectrum of the reaction mixture revealed only traces of **5b** (δ ^{31}P 92 ppm). The reaction was complete only in 1 year. The reaction mixture was treated with sulfur (20 mmol), diluted with benzene (20 ml), and filtered off. The filtrate was evaporated under reduced pressure to dryness and the residue was recrystallized.

^{1}H NMR ($CDCl_3$): δ (ppm) 7.17 (s, 4H, Ar), 3.15 (m, 16H, NCH_2), 2.41 (s, 3H, CH_3), 1.05 (t, $J = 6.9$ Hz, 24H, $NCH_2\underline{CH_3}$).

*3,5-Bis-(tetraethyldiamidothiophosphono)-4-benzyl-4H-1,2,4-triazole (**5c**)*

This compound was prepared analogously to **5b** from 4-benzyl-4*H*-1,2,4-triazole (**1c**) and $(Et_2N)_2PCl$ (Method **B**). In this case, the reaction was complete in 72 h.

^{1}H NMR (DMSO-d_6): δ (ppm) 7.27 (m, 3H, *m,p*-Ph), 7.10 (m, 2H, *o*-Ph), 6.24 (s, 2H, CH_2), 2.99 (m, 16H, NCH_2), 0.94 (bs, 24H, $NCH_2\underline{CH_3}$).

*(4-Methyl-5-phenyl-4H-1,2,4-triazol-3-yl)diphenylphosphine (**8**)*

To a stirred mixture of the triazole **7** (6 mmol), Et_3N (6 mmol), and pyridine (6 ml) was added Ph_2PCl (6 mmol). The reaction mixture was kept for 18 h, diluted with benzene (10 ml), and a precipitate was filtered off. The filtrate was evaporated to dryness under reduced pressure and the residue was recrystallized.

^{1}H NMR ($CDCl_3$): δ (ppm) 7.62 (m, 6H, *o*-Ph + *o*-Ph_2P), 7.49 (m, 3H, *m,p*-Ph), 7.40 (m, 6H, *m,p*-Ph_2P), 3.67 (s, 3H, CH_3).

*(1-Methyl-1H-1,2,4-triazol-5-yl)diphenylphosphine (**10**)*

To a mixture of the triazole **9** (12 mmol), Et_3N (12 mmol), and pyridine (12 ml) was added Ph_2PCl (12 mmol). The reaction mixture was kept at ambient temperature for 18 h, diluted with benzene (15 ml), and a precipitate was filtered off. The filtrate was evaporated to dryness under reduced pressure and the residue was recrystallized.

^{1}H NMR ($CDCl_3$): δ (ppm) 8.02 (s, 1H, 3-H), 7.40 (m, 10H, Ph_2P), 3.91 (s, 3H, CH_3).

*(1-Methyl-1,2,4-1H-triazol-5-yl)tetramethyldiamidophosphonite (**13**) and Bis-(1-methyl-1,2,4-1H-triazol-5-yl)dimethylamidophosphonite (**14**)*

To a stirred mixture of 1-methyl-1*H*-1,2,4-triazole (0.05 mol), Et_3N (0.05 mol), and pyridine (50 ml), maintained at −40°C, was added PCl_3 (0.1 mol). The reaction mixture was kept for 3 h at this temperature, then diluted with cold toluene (50 ml), and Me_2NH (0.5 mol) was added dropwise to it, over 20 min. After 1 h, the reaction mixture was filtered, the precipitate being washed with toluene (30 ml), the filtrate was evaporated under reduced pressure. Vacuum distillation of the residue afforded the phosphamides **13** and **14**.

13: ^{1}H NMR (C_6D_6): δ (ppm) 8.05 (s, 1H, 3-H), 3.48 (s, 3H, CH_3), 2.65 (d, $J = 9.6$ Hz, 12H, NCH_3).

14: ^{1}H NMR (C_6D_6): δ (ppm) 7.98 (s, 2H, 3-H), 3.49 (s, 6H, CH_3), 2.69 (d, $J = 10.2$ Hz, 6H, NCH_3).

*1-(2-Nitro-4-trifluoromethylphenyl)-1H-1,2,4-triazole (**15**)*

To a solution of 1,2,4-triazole (2.5 g, 36.2 mmol) in DMF (4.5 ml) was added 1-chloro-2-nitro-4-trifluoromethylbenzene (5 ml, 33.5 mmol). The reaction mixture was heated to 100–105°C, and freshly calcined, finely ground K_2CO_3 (8 g, 58 mmol) was added portionwise under stirring. Then the reaction mixture was stirred at 110–115°C for 0.5 h, cooled to room temperature, and poured into water (60 l). The crystalline solid that had precipitated was filtered off, washed with water, and recrystallized from EtOH/H_2O with addition of activated charcoal.

Yield 5.87 g (68%). mp = 70°C (EtOH/H_2O). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.81 (d, $J = 8.0$ Hz, 1H, H-6),

8.05 (dd, $J = 8.0$ and 1.6 Hz, 1H, H-5), 8.17 (s, 1H, triazole), 8.29 (d, $J = 1.6$ Hz, 1H, H-3), 8.49 (s, 1H, triazole). IR (KBr): 3150 (C—H), 1640, 1560 cm^{-1}. Anal calcd for $C_9H_5F_3N_4O_2$: C, 41.87%; H, 1.95%; N, 21.70%. Found: C, 42.10%; H, 1.9%; N, 21.82%.

*2-(1H-1,2,4-Triazol-1-yl)-5-trifluoromethyl-aniline (***16***)*

A mixture of the above-prepared nitrocompound **15** (4 g, 15.5 mmol), Fe powder (8 g, 0.143 mol), HOAc (40 ml), and EtOH (20 ml) was heated in a 0.25-l round-bottom flask equipped with a condenser until vigorous reaction took place. Then, the heating bath was removed and the mixture was allowed to boil. When boiling ceased, the reaction mixture was refluxed for 0.5 h, cooled to room temperature, and filtered under an atmosphere of argon. The filtrate was evaporated under reduced pressure. The dark-brown oily residue was dissolved in 150 ml of ethanol and treated with saturated aqueuos K_2CO_3 under vigorous shaking to provide a clear solution with Fe-containing lower layer. The solution was decanted and evaporated to dryness under reduced pressure. The solid residue was dissolved in dilute HCl. The resulting solution was treated with charcoal and stirred for 0.5 h, filtered, and basified with aqueous K_2CO_3. The crystalline solid that had formed was collected by filtration and washed with water to afford 2.93 g (83%) of the pure product.

mp = 122–123°C (heptane/toluene). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.88 (bs, 2H, NH_2), 7.06 (d, $J = 8.2$ Hz, 1H, H-5), 7.11 (s, 1H, H-3), 7.32 (d, $J = 8.2$ Hz, 1H, H-6), 8.19 (s, 1H, triazole), 8.42 (s, 1H, triazole). IR (KBr): 3455, 3340 (NH_2), 1650 cm^{-1}. Anal calcd for $C_9H_7F_3N_4$: C, 47.38%; H, 3.09%; N, 24.55%. Found: C, 46.99%; H, 4.18%; N, 24.24%.

*2-(1H-1,2,4-Triazol-1-yl)-1-(4-chlorophenyl-carboxamido)-5-trifluoromethylbenzene (***17***)*

A mixture of the aniline **16** (0.7 g, 3.07 mmol), *p*-ClC_6H_4COCl (0.39 ml, 3.07 mmol), and MeCN (10 ml) was refluxed for 1 h, and then evaporated to dryness under reduced pressure. The residue was recrystallized from EtOH/H_2O 3:2.

Yield 1.05 g (93%). mp = 178–179°C (EtOH/H_2O). ^{1}H NMR (DMSO-d_6): δ (ppm) 7.63 (d, $J = 9.0$ Hz, 2H, *m*-H COC_6H_4Cl), 7.81 (dd, $J = 8.7$ Hz and 1.5 Hz, 1H, H-5), 7.89 (d, $J = 9.0$ Hz, 2H, *o*-H COC_6H_4Cl), 7.95 (d, $J = 8.7$ Hz, 1H, H-6), 8.31 (s, 1H, triazole), 8.34 (bs, 1H, H-3), 9.11 (s, 1H, triazole). IR (KBr): 3340 (N—H), 1700 (C=O), 1610 cm^{-1}. Anal calcd for $C_{16}H_{10}ClF_3N_4O$: N, 15.28%; Cl, 9.67%. Found: N, 14.77%; Cl, 9.64%.

*5-(4-Chlorobenzoyl)-4-morpholino-4-thioxo-7-trifluoromethyl-4,5-dihydrobenzo[e][1,2,4]-triazolo[5,1-c][1,4,2]diazaphosphinine (***19a***)*

Phosphorus tribromide (0.3 ml, 3.16 mmol) was added to a stirred mixture of **17** (1.16 g, 3.16 mmol), triethylamine (0.9 ml, 6.46 mmol) and pyridine (15 ml) at −25°C. The reaction mixture was stirred for 1 h on a cooling bath, the temperature being allowed to rise slowly to 0°C, and stirring was continued for a futher 10 h at room temperature. To thus prepared solution of **18** (δ^{31}P 36.6 ppm), were subsequently added triethylamine (0.45 ml, 3.23 mmol), morpholine (0.27 ml, 3.10 mmol), and sulfur (120 mg, 3.74 mmol). The reaction mixture was stirred for 6 h at 85°C, cooled to room temperature and diluted with toluene (20 ml). The precipitate of the salts was filtered off, and the filtrate was evaporated to dryness under reduced pressure. The residue was triturated with MeOH (5 ml) to yield crystalline material, which was then filtered off and washed with cold MeOH (3 ml).

^{1}H NMR ($CDCl_3$): δ (ppm) 2.98 (m, 2H, NCH_2), 3.45 (m, 2H, NCH_2), 3.68 (m, 2H, OCH_2), 3.80 (m, 2H, OCH_2), 7.13 (s, 1H, H-6), 7.40 (d, $J = 8.4$ Hz, 1H, *m*-H COC_6H_4Cl), 7.58...7.63 (m, 3H, *o*-H COC_6H_4Cl + H-8), 8.22 (d, $J = 8.4$ Hz, 1H, H-9), 8.34 (d, $J = 1.2$ Hz, 1H, H-2). IR (KBr): 2985, 2940, 2880 (CH_2), 1700 (C=O), 1600 cm^{-1}.

*4-Chloro-N-[2-{5-[dimorpholinophosphothioyl]-1H-1,2,4-triazole-1-yl}-5-trifluoromethylphenyl] benzamide (***21***)*

To a solution of **18** prepared as described above, were subsequently added morpholine (1.1 ml, 12.64 mmol) and sulfur (110 mg, 3.43 mmol). The work-up procedure described previously for **19a** followed, after 10 h stirring of the reaction mixture at room temperature.

^{1}H NMR ($CDCl_3$): δ (ppm) 3.13 (m, 8H, NCH_2), 3.54 (m, 8H, OCH_2), 7.46 (d, $J = 8.4$ Hz, 2H, *m*-H COC_6H_4Cl), 7.57 (1H, dd, $J = 8.4$ Hz and 1.5 Hz, H-4), 7.70 (d, $J = 8.4$ Hz, 2H, *o*-H COC_6H_4Cl), 8.07 (d, $J = 8.4$ Hz, 1H, H-3), 8.31 (s, 1H, triazole), 8.74 (d, $J = 1.5$ Hz, 1H, H-6), 8.88 (1H, s, CONH). IR (KBr): 3440 (N—H), 2900, 2915, 2875 (CH_2), 1700 (C=O), 1610 cm^{-1}.

*2-(5-[Dimorpholinophosphotioyl]-1H-1,2, 4-triazole-1-yl)-5-trifluoromethylaniline (***22***)*

A solution of **19** (0.60 g, 1.0 mmol) and KOH (120 mg, 2.14 mmol) in MeOH (7 ml) was refluxed for 24 h, cooled to room temperature, and diluted with water

(70 ml). The precipitate of **21** that had formed was filtered off and washed with water.

^{1}H NMR ($CDCl_3$): δ (ppm) 3.17 (m, 8H, N—CH_2), 3.60 (m, 8H, O—CH_2), 4.08 (s, 2H, NH_2), 7.09...7.11 (m, 2H, H-4 + H-6), 7.71 (d, $J = 8.4$ Hz, 1H, H-3), 8.23 (s, 1H, triazole). IR (KBr): 3450, 3350 (NH_2), 2920, 2880 (CH_2), 1640 cm^{-1}.

*5-(4-Chlorobenzoyl)-4-phenyl-4-thioxo-7-trifluromethyl-4,5-dihydrobenzo[e][1,2,4]-triazole[5,1-c][1,4,2]diazaphosphinine (***19b***)*

Dibromophenylphosphine (0.5 ml, 3.50 mmol) was added to a stirred mixture of **17** (1.28 g, 3.49 mmol), triethylamine (1.0 ml, 7.2 mmol), and pyridine (15 ml) at −25°C. The reaction mixture was stirred for 1 h on a cooling bath, the temperature being allowed to rise slowly to 0°C, and then stirred for an additional 48 h at room temperature. To thus prepared solution of **23** (δ^{31}P 4.4 ppm) was added sulfur (120 mg, 3.74 mmol). The reaction mixture was then stirred for 6 h at 85°C and worked up as described for **19a**.

^{1}H NMR (DMSO-d6): δ (ppm) 7.44 (d, $J = 8.1$ Hz, 2H, *m*-H COC_6H_4Cl), 7.56...7.63 (m, 3H, *m*-H Ph + H-6), 7.68...7.74 (m, 3H, *p*-H Ph + *o*-H COC_6H_4Cl), 7.85 (d, $J = 9.0$ Hz, 1H, H-8), 8.19 (dd, $J = 7.5$ Hz and 17.1 Hz, 2H, *o*-H Ph), 8.36 (d, $J = 9.0$ Hz, 1H, H-9), 8.70 (s, 1H, H-2). IR (KBr): 1700 (C=O), 1600 cm^{-1}.

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