was washed with benzene. The resulting solution was extracted with chloroform, and the chloroform extract was washed with water, dried, and concentrated. The crude product was chromatographed on silica gel with 1:10 chloroform–hexane as the eluant to afford 403 mg (73%) of 1-thiaphenalene. Further purification by sublimation at 60 °C (0.03 mmHg) yielded light yellow crystals of **2**: mp 120 °C (lit. mp 124 °C,[3] 120–122 °C[4]); ^{1}H NMR ($CDCl_3$) δ 6.10 (d, 1 H, J = 9.6 Hz), 6.41 (d, 1 H, J = 9.6 Hz), 6.69 (dd, 1 H, J = 7.1, 2 Hz), 6.82–7.34 (m, 5 H); mass spectrum, m/e (relative intensity) 186 (5), 185 (13), 184 (100), 183 (12), 152 (37), 151 (8), 139 (31); IR (CCl_4) 3050, 1635, 1570, 1435, 1377, 1368, 1330, 960 cm^{-1}. Anal. Calcd for $C_{12}H_8S$: C, 78.26; H, 4.35; S, 17.39. Found: C, 78.39; H, 4.31; S, 17.52.

1-Thiaphenalene Hexafluorophosphate. Into a H-tube fitted with a medium-porosity glass frit in the bridge and containing 0.1 M tetrabutylammonium hexafluorophosphate in methylene chloride was placed 5 mg of **2** in one side of the tube. The tube was then attached to platinum electrodes connected to a 3-V battery (positive electrode in the side containing **2**). After a period of 7 days, the 1-thiaphenalene hexafluorophosphate was collected from the electrode. It was washed twice with a small portion of acetonitrile to give a black powder. Anal. Calcd for $C_{12}H_8F_6PS$: C, 43.77; H, 2.43. Found: C, 44.71; H, 2.64. The lack of material precluded the possibility of obtaining duplicate or more accurate analysis.

Acknowledgment. We thank Dr. D. O. Cowan, Dr. MacRae Maxfield, and Mr, James Stokes at the Johns Hopkins University for their helpful assistance with the physical measurements. Partial support of this research by the National Science Foundation (Grant No. CHE 76-82122) is acknowledged with pleasure.

Registry No. **2**, 203-93-0; **2** radical cation PF_6^-, 78167-10-9; **3**, 78167-11-0; **4**, 78167-12-1; **5**, 78167-13-2; **6**, 78167-14-3; **7**, 78167-15-4; **8**, 78167-16-5.

(Dimethylthiocarbamoyl)thio Group as a Protecting Group of Phosphates in Oligonucleotide Synthesis via the Phosphotriester Approach[1]

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It has been shown by several workers[2] that a nucleoside 3′-phosphotriester is a key intermediate in the synthesis of oligonucleotide by the improved phosphotriester method. Recently, it has been demonstrated in our laboratory that 5′-*O*-(dimethoxytrityl)-2′-*O*-tetrahydropyranylnucleoside 3′-(4-chlorophenyl 5-chloro-8-quinolyl) phosphates are key intermediates in the synthesis of Rous Sarcoma virus 35S RNA by the improved phosphotriester method.[3] More recently, we have found that 5′-*O*-(methoxytrityl)deoxyribonucleoside 3′-[2-cyanoethyl *S*-(dimethylthiocarbamoyl) thiophosphates] **2** are key intermediates in the synthesis of deoxyribonucleotides by the improved phosphotriester method. The (dimethylthiocarbamoyl)thio group is stable to acid and alkali solutions,[4] removal being achieved specifically by treatment with boron trifluoride in a mixture of dioxane and water (9:1 v/v).

Table I. Reaction Conditions and Yields for the Synthesis of Nucleoside 3′-Phosphotriesters **2**[a]

step 1				step 2		
mmol	pCe, mmol	QS, mmol	time, h	$(Me_2NCSS)_2$-Ph_3P, mmol	time, h	yield, %
MMTrT						
0.50	0.55	1.10	12	0.55	24	21
0.50	0.55	1.10	12	1.65	24	68
0.50	0.55	1.65	12	1.65	24	35
0.50	0.45	0.90	12	2.25	24	67
1.00	1.10	2.20	12	5.50	24	88
d-MMTr(anC)						
1.00	1.10	2.20	12	5.50	24	85
d-MMTr(bzA)						
1.00	1.10	2.20	12	5.50	24	79
d-MMTr(ibuG)						
1.00	1.10	2.20	18	5.50	24	68

[a] MMTr = monomethoxytrityl; pCe = 2-cyanoethyl phosphate; QS = 8-quinolinesulfonyl chloride.

In the present paper, we describe the synthesis of deoxyribooligonucleotides using the (dimethylthiocarbamoyl)thio group as a new protecting group on phosphates in internucleotidic bonds.

We first examined preparation of 5′-*O*-(methoxytrityl)deoxyribonucleoside 3′-[2-cyanoethyl *S*-(dimethylthiocarbamoyl) thiophosphates] **2**.

5′-*O*-(Methoxytrityl)thymidine (1.0 mmol) was treated with 2-cyanoethyl phosphate (1.1 mmol) in the presence of 8-quinolinesulfonyl chloride (QS)[5] (2.2 mmol) in dry pyridine. After 12 h, TLC shows that the phosphorylation was completed. To the reaction mixture were added bis(dimethylthiocarbamoyl) disulfide (5.5 mmol) and triphenylphosphine (5.5 mmol). The mixture was kept for 24 h at room temperature. After the usual workup, the fully protected mononucleotide **2a** was isolated in high yield by silica gel column chromatography (see Table I). In the above reactions, the use of a slight excess of nucleoside over 2-cyanoethyl phosphate gave a poorer yield of **2a**. Furthermore, when the isolated phosphodiester **1a** was allowed to react with bis(dimethylthiocarbamoyl) disulfide and triphenylphosphine, the yield of **2a** decreased to 45% yield. From above facts, when we speculate on the mechanism for the phosphorylation, the following scheme may be most plausible at present (Scheme I).

We next examined the synthesis of dinucleotide **5** and trinucleotide **7** by using **2**. The phosphotriester **2a** was treated with 2% benzenesulfonic acid in a mixture of di-

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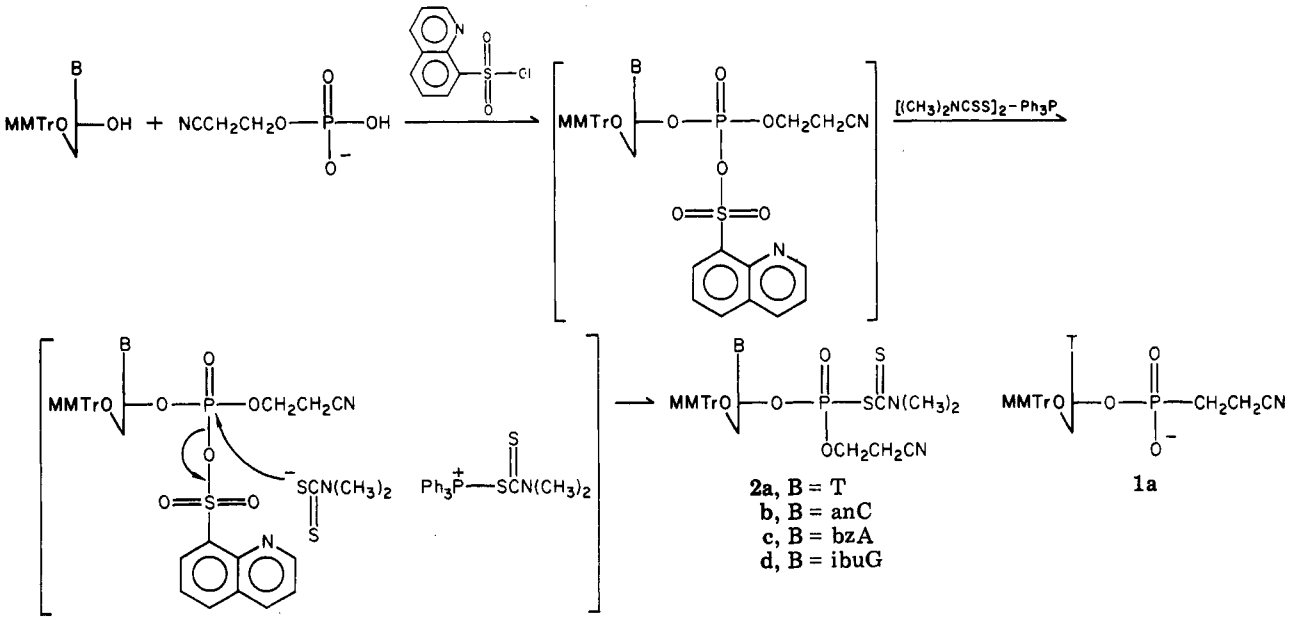
(3) Takaku, H.; Nomoto, T.; Kamaike, K. *Nucleic Acid Symp. Ser.* **1980**, *No. 8*, s91.

(4) The (dimethylthiocarbamoyl)thio group was stable to acid and alkali solutions (hydrochloric acid, pH 2, and aqueous ammonia, 6 M) over a period of 48 h.

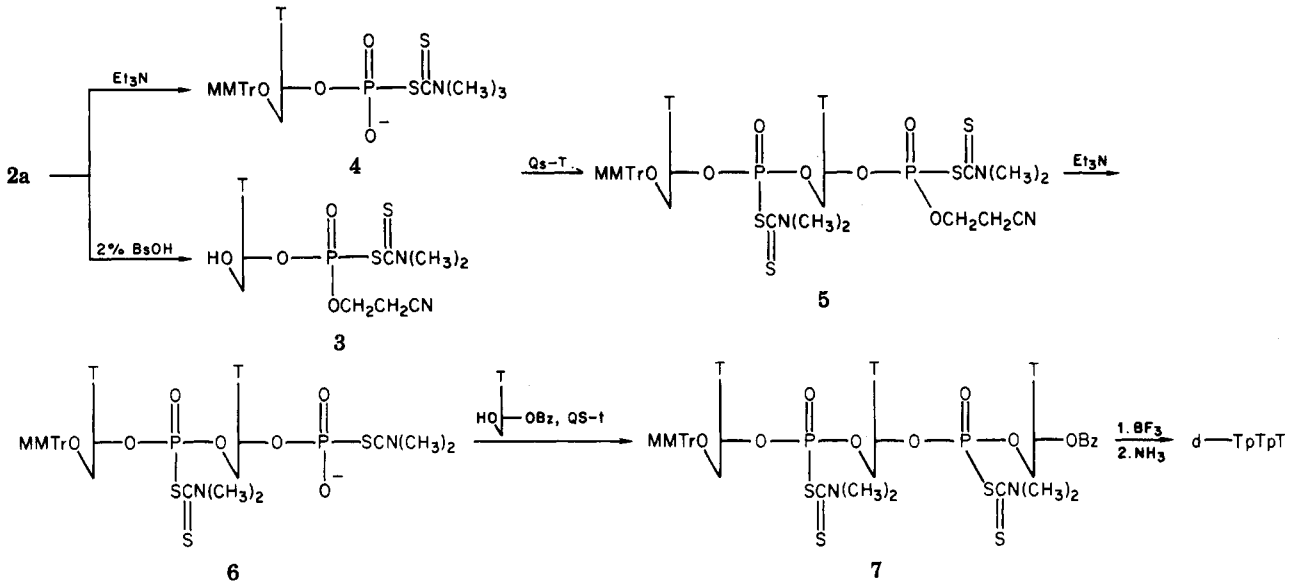
(5) (a) Takaku, H.; Yoshida, M.; Kato, M.; Hata, T. *Chem. Lett.* **1979**, 811. (b) Takaku, H.; Kato, M.; Yoshida, M.; Ymaguchi, R. *J. Org. Chem.* **1980**, *45*, 3347.

0022-3263/81/1946-4062$01.25/0

Scheme I



Scheme II[a]



[a] BsOH = benzenesulfonic acid; QS-t = 8-(quinolinesulfonyl)tetrazole.

oxane and methanol (7:3 v/v) for 25 min at 0 °C to give **3**[6] (Scheme II). The 5′-hydroxyl nucleotide **3a** was isolated in 88% yield by precipitation with *n*-hexane and in the subsequent coupling reaction without further purification. On the other hand, the phosphotriester **3** (0.53 mmol) was treated with triethylamine (0.5 mL) in dry pyridine (1.5 mL) for 6 h at 25 °C. Following removal of most of the solvent in vacuo, the residue was rendered anhydrous by repeated coevaporation with dry pyridine. The phosphodiester **4** thus obtained was dissolved in dry pyridine and then **3** (0.35 mmol) and (8-quinolinesulfonyl)tetrazole (QS-t) were added. After 1 h, the precipitated 8-quinolinesulfonic acid[5] was removed by filtration. The filtrate was quenched with ice–water and extracted with methylene chloride, and the extract was back-washed with triethylammonium bicarbonate (0.1 M, pH 7.5). The methylene chloride was evaporated in vacuo. The residue was dissolved in methylene chloride and chromatographed on a silica gel column. The fully protected dinucleotide **5** was isolated 65% yield by eluting the column with methylene chloride–methanol (94:6 v/v).

The fully protected dinucleotide **5** (0.3 mmol) thus obtained was treated with triethylamine to cleave the 2-cyanoethyl group, and the corresponding phosphodiester **6** was condensed with 3′-*O*-benzoylthymidine (0.45 mmol) and QS-t for 1 h to give the fully protected trinucleotide **7** in 58% yield.

Complete deblocking of the desired products **2**, **5**, and **7** was performed as follows. The 2-cyanoethyl group was removed by treatment with triethylamine for 6 h at 25 °C. The reaction mixture was evaporated in vacuo, and the residue was treated with boron trifluoride in a mixture of dioxane and water (9:1 v/v) for 1 h at room temperature.[7]

(6) Stawinski, J.; Hozumi, T.; Narang, S. A.; Bahl, C. P.; Wu, R. *Nucleic Acids Res.* **1977**, *4*, 353.

(7) When 5′-*O*-(methoxytrityl)-N^6-benzoyldeoxyadenosine 3′-[2-cyanoethyl *S*-(dimethylthiocarbamoyl) thiophosphate] **2c** was treated with boron trifluoride etherate in a mixture of dioxane and water (9:1 v/v) for 5 h at room temperature, N^6-benzoyldeoxyadenosin-3′-yl 2-cyanoethyl phosphate was obtained in 92% yield along with the depurinated product (8%).

Table II. Characterization of Deoxyribooligonucleotides

compd	R_f A[a]	R_f B[b]	enzyme degradation: nuclease P1	enzyme degradation: spleen phosphodiesterase
d-Tp	0.15	0.30		
d-Cp	0.12	0.26		
d-Ap	0.16	0.30		
d-Gp	0.15	0.31		
d-TpTp	0.07	0.13	d-pT/T (0.9/1.0)	d-Tp
d-TpTpTp	0.11	0.20	d-pT/T (1.98/1.0)	d-Tp/T (2.08/1.0)

[a] Solvent A: 2-propanol-concentrated ammonia-water (7:1:2 v/v). [b] Solvent B: n-butanol-glacial acetic acid-water (5:2:3 v/v).

(Dimethylthiocarbamoyl)thio and methoxytrityl groups are quantitatively removed within this period of time. This deprotection sequence is very clean, and only the desired nucleotide products are obtained in 84–89% yields. The structures of the deblocked products were confirmed by complete degestion with nuclease P1 and spleen phosphodiesterase (see Table II).

The results described in this paper demonstrate the efficiency of the (dimethylthiocarbamoyl)thio group as a phosphate protecting group for the oligonucleotide synthesis via the phosphotriester approach.

Experimental Section

All general methods for chromatography, paper electrophoresis, and enzyme analyses are described in ref 5 and 8. Merck DC-Alufolien Cellulose F_{254} sheets were used for TLC. HPLC was carried out on a Finepak C_{18} column which was eluted with 10% acetonitrile in triethylammonium acetate (pH 7.0). The nucleosides were prepared according to literature procedures.[9]

Synthesis of 5′-*O*-(Methoxytrityl)nucleoside 3′-[2-cyanoethyl *S*-(dimethylthiocarbamoyl) thiophosphate] (2). The 5′-*O*-(methoxytrityl) nucleoside (1 mmol) and 2-cyanoethyl phosphate (1.1 mmol) were rendered anhydrous by coevaporation with dry pyridine and treated with 8-quinolinesulfonyl chloride (QS; 502 mg, 2.2 mmol) in dry pyridine (15 mL). After 12 h, bis(dimethylthiocarbamoyl) disulfide[10] (1.32 g, 5.5 mmol) and triphenylphosphine (1.44 g, 5.5 mmol) were added, and the reaction mixture was stirred for 24 h at room temperature. The reaction was quenched with ice–water (5 mL), and the product was extracted with methylene chloride (3 × 50 mL). The methylene chloride extract was washed with 0.1 M triethylammonium bicarbonate (pH 7.5, 3 × 40 mL) and water (60 mL), dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The residue was dissolved in a small amount of methylene chloride and chromatographed on a silica gel column (30 × 2.5 cm). The column eluted with a stepwise gradient of methanol (0–6%) in methylene chloride. The products **2** were precipitated with n-hexane–ether (9:1 v/v) from its solution in methylene chloride (see Table I).

(a) 5′-*O*-(Methoxytrityl)thymidine 3′-[2-cyanoethyl *S*-(dimethylthiocarbamoyl) thiophosphate] (2a): UV (methanol) λ_{max} 281 nm (sh), 265, 230, λ_{min} 248; R_f 0.44 (CH_2Cl_2–MeOH, 9:1 v/v), 0.38 (CH_2Cl_2–MeOH, 92:8 v/v). Anal. Calcd for $C_{36}H_{39}N_4O_8PS_2$: C, 57.59; H, 5.24; N, 7.46. Found: C, 57.47; H, 5.36; N, 7.51.

(b) 5′-*O*-(Methoxytrityl)-*N*⁴-anysoyldeoxycytidine 3′-[2-cyanoethyl *S*-(dimethylthiocarbamoyl) thiophosphate] (2b): UV (methanol) λ_{max} 302 nm, 285, 230, λ_{min} 292, 248; R_f 0.48 (CH_2Cl_2–MeOH, 9:1 v/v), 0.41 (CH_2Cl_2–MeOH, 9:1 v/v). Anal. Calcd for $C_{43}H_{42}N_5O_9PS_2$: C, 59.51; H, 4.88; N, 8.07. Found: C, 59.44; H, 4.91; N, 8.06.

(c) 5′-*O*-(Methoxytrityl)-*N*⁶-benzoyldeoxyadenosine 3′-[2-cyanoethyl *S*-(dimethylthiocarbamoyl) thiophosphate] (2c): UV (methanol) λ_{max} 281 nm 233, λ_{min} 248; R_f 0.51 (CH_2Cl_2–MeOH, 9:1, v/v), 0.45 (CH_2Cl_2–MeOH, 92:8 v/v). Anal. Calcd for $C_{43}H_{42}N_7O_7PS_2$: C, 59.78; H, 5.09; N, 11.14. Found: C, 59.51; H, 5.09; N, 11.43.

(d) 5′-*O*-(Methoxytrityl)-*N*²-isobutylylguanosine 3′-[2-cyanoethyl *S*-(dimethylthiocarbamoyl) thiophosphate] (2d): UV (methanol) λ_{max} 282 nm, 261 (sh), 255, 235, λ_{min} 273, 243; R_f 0.50 (CH_2Cl_2–MeOH, 9:1 v/v), 0.43 (CH_2Cl_2–MeOH, 92:8 v/v). Anal. Calcd for $C_{40}H_{44}N_7O_8PS_2$: C, 56.79; H, 5.24; N, 11.59. Found: C, 56.84; H, 5.19; N, 11.67.

Detritylation of the Fully Protected Nucleotide 2a. The fully protected nucleotide **2a** was treated with 2% benzenesulfonic acid in methylene chloride–methanol (7:3 v/v) for 25 min at 0 °C. After the trityl cleavage was completed, the mixture was neutralized with 5% sodium carbonate solution and transferred into methylene chloride. The methylene chloride extract was washed with water and then dried over anhydrous sodium sulfate. The residue remaining after removal of methylene chloride was precipitated from n-hexane–ether (9:1 v/v) and used as the 5′-hydroxyl component in the next condensation without further purification.

Synthesis of the Fully Protected Dinucleotide 5. The phosphotriester **2a** (398 mg, 0.53 mmol) was treated with triethylamine (0.5 mL) in dry pyridine (1.5 mL) for 6 h at 25 °C. The solution was evaporated in vacuo, and the residue was rendered anhydrous by repeated coevaporation with dry pyridine. The phosphodiester **4** thus obtained was dissolved in dry pyridine (3 mL) and then 5′-hydroxyl nucleotide **3** (167 mg, 0.35 mmol) and (8-quinolinesulfonyl)tetrazole (QS-t; 279 mg, 1.06 mmol) were added. After 1 h, 8-quinolinesulfonic acid was removed by filtration. The filtrate was quenched with ice–water (1 mL) and extracted with methylene chloride (3 × 20 mL), and the extract was back-washed with 0.1 M triethylammonium bicarbonate (pH 7.5, 2 × 30 mL) and then with water (30 mL). The methylene chloride was dried over anhydrous sodium sulfate and evaporated with addition of toluene. The residue was dissolved in a small amount of methylene chloride and chromatographed on silica gel column. The column was eluted with a stepwise gradient of methanol (0–5%) in methylene chloride. The appropriate fractions were evaporated to give **5** which was isolated (263 mg, 65%) by precipitation from n-hexane–ether (9:1 v/v): UV (methanol) λ_{max} nm (sh), 265 (ε 20.500), 230, λ_{min} 248; R_f 0.46 (CH_2Cl_2–MeOH, 9:1 v/v), 0.34 (CH_2Cl_2–MeOH, 92:8 v/v). Anal. Calcd for $C_{49}H_{57}N_7O_{14}P_2S_4$: C, 50.81; H, 4.96; N, 8.46. Found: C, 50.79; H, 4.90; N, 8.51.

Synthesis of the Fully Protected Trinucleotide 7. The phosphodiester **6** obtained from **5** (347 mg, 0.3 mmol) by treatment with triethylamine (0.5 mL) as described for **5** was combined with 3′-*O*-benzoylthymidine (77 mg, 0.45 mmol), rendered anhydrous by coevaporation with dry pyridine, and then treated with QS-t (158 mg, 0.6 mmol) in dry pyridine (2 mL) for 1 h at room temperature. 8-Quinolinesulfonic acid was removed by filtration. The filtrate was quenched with ice–water (1 mL), followed by extraction with methylene chloride (3 × 10 mL). The methylene chloride extract was washed with 0.1 M triethylammonium bicarbonate (pH 7.5) and then with water, dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure to a gum. The gum was dissolved in a small amount of methylene chloride and chromatographed on a silica gel column. The column was eluted with a stepwise gradient of methanol (0–6%) in methylene chloride. The appropriate fractions were evaporated to give **7** which was isolated (262 mg, 58%) by precipitation from n-hexane–ether (9:1 v/v): UV (methanol) λ_{max} 284 nm (sh), 266, 230, λ_{min} 246; R_f 0.40 (CH_2Cl_2–MeOH, 9:1 v/v), 0.32 (CH_2Cl_2–MeOH, 92:8 v/v).

Complete Deprotection of Oligonucleotides. The fully protected oligonucleotides (0.05 mmol) were dissolved in a mixture of dioxane and water (9:1 v/v, 5 mL), and then boron trifluoride etherate (0.5 mmol) was added at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred for 5 h. The solution was passed through a Dowex 50W-X2 (pyridinium

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(9) (a) Schaller, H.; Weimann, G.; Lerch, B.; Khorana, H. G. *J. Am. Chem. Soc.* **1963**, *85*, 3841. (b) Büchi, H.; Khorana, H. G. *J. Mol. Chem.* **1972**, *72*, 251.

(10) Rothstein, R.; Binovic, K. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 561.

form) ion exchange column. The eluant was collected and concentrated in vacuo. The residue was treated with methanolic ammonia for 48 h at room temperature. The solution was evaporated in vacuo, and the product was isolated by paper chromatography (2-propanol–concentrated ammonia–water (7:1:2 v/v). Yields were 84–89% as determined spectrophotometrically. Characterization of the deprotected oligonucleotides are collected Table II.

Registry No. **1a**, 78456-41-4; **1b**, 78479-39-7; **1c**, 78456-42-5; **1d**, 78456-43-6; **2a**, 78512-47-7; **2b**, 78512-48-8; **2c**, 78456-44-7; **2d**, 78456-45-8; **3**, 78513-23-2; **4**, 78512-49-9; **5**, 70007-96-4; **6**, 78456-46-9; **7**, 78456-47-0; 2-cyanoethyl phosphate, 2212-88-6; bis(dimethylthiocarbamoyl) disulfide, 137-26-8; 5′-*O*-(methoxytrityl)thymidine, 42926-80-7; 5′-*O*-(methoxytrityl)-N^4-anisoyldeoxycytidine, 57361-91-8; 5′-*O*-(methoxytrityl)-N^6-benzoyldeoxyadenosine, 24816-13-5; 5′-*O*-(methoxytrityl)-N^2-isobutyryldeoxyguanosine, 59321-92-5; 3′-*O*-benzoylthymidine, 17331-53-2; N^6-benzoyldeoxyadenosin-3′-yl 2-cyanoethyl phosphate, 78456-48-1; *d*-Tp, 2642-43-5; *d*-Cp, 6220-63-9; *d*-Ap, 15731-72-3; *d*-Gp, 6220-62-8; *d*-TpTp, 2476-56-4; *d*-TpTpTp, 4712-59-8.

Nonclassical Heteropentalenes Containing the Selenodiazole, Thiatriazole, and Selenotriazole Ring Systems[1]

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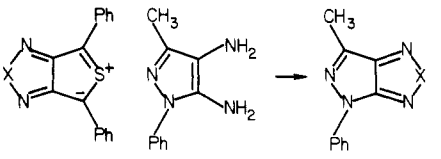
Heteropentalenes containing a "nonclassical" thiophene nucleus have been found to undergo a variety of cycloaddition reactions,[2] often leading to unexpected products.[3] The most interesting cycloaddition properties exist in those systems containing only one heteroatom in each of the two fused rings, additional heteroatoms resulting in increased stability and reduced chemical reactivity. Incorporation of a nitrogen atom at the ring junction of the bicyclic system also has a pronounced effect on the stability and properties of the resultant systems. In this publication evidence is presented to substantiate further the above generalizations.

Diphenylthieno[3,4-*c*][1,2,5]thiadiazole (1, X = S) undergoes[4] cycloaddition with electron-deficient dipolarophiles across the thiocarbonyl ylide dipole only. No reaction was observed at the N^-—S^+=N dipole. In this instance extrusion of sulfur occurs with formation of the corresponding benzothiadiazoles.[3,4] The corresponding diphenylthieno[3,4-*c*][1,2,5]oxadiazole (1, X = O) also undergoes reaction with acetylenic dipolarophiles across the thiocarbonyl ylide but in this system, in addition to the benzooxadiazole, an isoxazolyl dihydrothiophene derivative is formed by fission of the oxadiazole ring. An intermediate nitrile oxide then undergoes additional reaction with another molecule of the acetylene.[3] In contrast, the corresponding 4,6-diphenyl-2-methylthieno[3,4-*c*]-[1,2,3]triazole (1, X = NCH_3) did not undergo[5] cycloaddition with a variety of electron-deficient dipolarophiles. The 1,2,5-thiadiazolo[3,4-*c*]thiadiazole prepared[6] from 3,4-diamino-1,2,5-thiadiazole and sulfur monochloride in DMF proved to be a relatively stable ring system whose bond lengths indicated that it should be considered an heteroaromatic compound. It did not undergo cycloaddition with a variety of electron-deficient dipolarophiles.

We have found that reaction of 4,5-diamino-1-phenyl-3-methylpyrazole dihydrochloride (2) with sulfur monochloride readily afforded 6-methyl-4-phenylpyrazolo[3,4-*c*][1,2,5]thiadiazole (3, X = S). The structure of 3 (X =

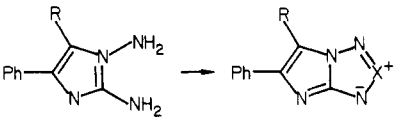


1 2 3

S) followed from its analytical and spectral data which are listed in Table I. No evidence of cycloadditions with dipolarophiles was found for 3 (X = S).

1,2,5-Selenadiazoles are also readily available from 1,2-diamino compounds and selenium dioxide or selenium monochloride, this route being particularly suited to the synthesis of condensed aromatic systems.[8] Reaction of 2 with selenium dioxide readily gave 6-methyl-4-phenylpyrazolo[3,4-*c*][1,2,5]selenadiazole (3, X = Se) whose structure was established on the basis of its analytical and spectral data shown in Table I.

Applying similar reactions to appropriately substituted 1,2-diaminoimidazoles allows the introduction of a nitrogen atom at a ring junction position. Thus 1,2-diamino-4,5-diphenylimidazole[9] (4, R = Ph) was treated with thionyl chloride in hot pyridine solution and afforded 5,6-diphenylimidazolo[1,2-*c*]thiatriazole (5, X = S, R = Ph) as orange needles (68%). The structure of 5 (X = S, R =



4 5

Ph) was established on the basis of its analytical and spectral data. Its infrared spectrum was devoid of NH absorptions and its NMR spectrum consisted of a complex aromatic multiplet centered at δ 7.4. The molecular ion *m/e* 278 was the most abundant ion in the spectrum and an [M + 2] ion was consistent with the presence of one sulfur atom. 5-Phenylimidazolo[1,2-*c*]thiatriazole (5, X = S, R = H) was prepared in a similar manner from 1,2-diamino-4-phenylimidazole (4, R = H) and thionyl chloride/pyridine except that a reaction temperature of 0 °C was required. It was obtained after chromatography as yellow needles (40%), and it proved to be considerably less stable to heat than the diphenyl analogue. Its structure was consistent with its analytical and spectral data, the

(1) Abstracted in part from the Ph.D. Thesis (R.C., 1980) and the M.S. Thesis (R.J.D., 1978), Rensselaer Polytechnic Institute.

(2) For a summary of these reactions, see Cava, M. P.; Lakshmikantham, M. V. *Acc. Chem. Res.* **1975**, *8*, 139. Potts, K. T. "Special Topics in Heterocyclic Chemistry"; Weissberger, A., Taylor, E. C., Eds.; Wiley: New York, 1977; Chapter 6. Ramsden, C. A. *Tetrahedron* **1977**, *33*, 3203.

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