Table I. Physical Properties of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NX)$ Complexes

	I, X = S	II, X = O
Color	Red-violet	Orange-red
Mp, °C	68.0–69.0	69.5–70.5
ν(CO), cm^{-1} (in hexane)[a]	2033 (s), 1962 (s)	2028 (s), 1955 (s)
ν(NX), cm^{-1} (in hexane)[a]	1180 (s)	1713 (s)
^1H NMR, δ (ppm) (in $CDCl_3$)[b]	5.08	5.03
^{13}C NMR, δ (ppm) (in $CDCl_3$)[b]	92.75 (C_5H_5)	90.76 (C_5H_5)
	239.43 (CO)	237.63 (CO)

[a] Recorded on a Perkin-Elmer 457 spectrophotometer and calibrated with the 1601-cm^{-1} band of polystyrene film. [b] ^1H and ^{13}C NMR spectra were recorded on Varian Associates T60 and CFT20 spectrometers, respectively, with Me_4Si being employed as an internal standard. The indicated chemical shifts are downfield from Me_4Si.

Table II. Low-Resolution Mass Spectral Data for $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NX)$ Complexes[a]

I, X = S			II, X = O	
m/e	Rel abundance	Assignment[b]	Rel abundance	*m/e*
219	36	$C_5H_5Cr(CO)_2(NX)^+$	26	203
191	8	$C_5H_5Cr(CO)(NX)^+$	21	175
163	74	$C_5H_5Cr(NX)^+$	13	147
117	100	$C_5H_5Cr^+$	100	117
52	63	Cr^+	37	52

[a] Obtained at 70 eV on an Atlas CH4B spectrometer using the direct-insertion method at room temperature. [b] The assignments involve the most abundant naturally occurring isotopes in each fragment.

those of II, thereby suggesting that the NS ligand is more effective in removing electron density from the central metal than is the NO ligand.[6] The Cr–(NS) bond in I also appears to be somewhat stronger than the Cr–(NO) bond in ii, as evidenced by the mass spectral data displayed in Table II. While both complexes exhibit fragmentation patterns corresponding to the sequential loss of ligands and the common base peak can be assigned to the $C_5H_5Cr^+$ ion, the $C_5H_5Cr(NS)^+$ ion is markedly more abundant in the mass spectrum of I than is the $C_5H_5Cr(NO)^+$ ion in the spectrum of II.

The NMR data of compounds I and II (Table I) provide an interesting contrast. The ^1H NMR spectrum of I consists of a single sharp peak which occurs at a slightly lower field than the corresponding absorption due to the cyclopentadienyl protons of II. Similarly, the ^{13}C NMR chemical shifts of the cyclopentadienyl and carbonyl carbons are further downfield from Me_4Si for complex I. A comparable downfield shift for $\delta(^{13}C_5H_5)$ has previously been observed[7] when a CO group in $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ (isoelectronic with II) has been replaced by a CS group to give $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ (isoelectronic with I). However, such a substitution also results in an upfield shift of $\delta(^{13}CO)$ which is exactly opposite to the effect that we observe in going from II to I. Rather than speculate on the factors responsible for this apparent anomaly, we have initiated single-crystal x-ray diffraction studies of I and II to ascertain the mode of linkage of the NO and NS groups in the two complexes. This information is essential for any future theoretical interpretation of the different electron-donating and electron-accepting abilities of the two ligands.

The reaction employed to prepare I resembles a procedure that we have previously used[8] to synthesize various organometallic nitrosyl complexes, namely the treatment of organometallic carbonyl anions with nitrosyl chloride, ClNO. Indeed, we believe that an important feature of our preparation of I is that in THF the trithiazyl trichloride reagent probably exists as a solvated monomer, $NSCl(THF)_x$. However, our attempts to prepare other organometallic thionitrosyl complexes by this route have not succeeded as yet because $S_3N_3Cl_3$ appears to be a stronger oxidizing agent than ClNO. For instance, treatment of the more nucleophilic anions[9] $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ (M = Mo or W) with $S_3N_3Cl_3$ in THF at −78 °C results in the formation of $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (III) and $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ (IV) as the only isolable organometallic products in yields of ~25 and ~15% (based on M), respectively. III is probably formed by the oxidation of the anionic reactant and IV could result from the reaction of III with $NSCl(THF)_x$ in a manner somewhat analogous to that reported[1] for ClNO. Consistent with this interpretation is the fact that $[Mn(CO)_5]^-$ is simply oxidized to $Mn_2(CO)_{10}$ by $S_3N_3Cl_3$ in THF.

Acknowledgments. We are grateful to the National Research Council of Canada (Grant A5885) for support of this research and to Professor N. L. Paddock for numerous stimulating conversations.

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An Intramolecular Model of 1,3-Dipolar Cycloaddition to the 5,6 Double Bond of a Pyrimidine Nucleoside. A New Route to the Regiospecific Synthesis of 4-Substituted Triazole Reversed Nucleosides

Sir:

$[_2\pi + _2\pi]$ photodimerization[1,2] and photocycloaddition of pyrimidines to electron-rich monoolefins[3] have been extensively studied in terms of photochemical transformation of natural nucleic acid and preparative chemistry aiming at effective carbon–carbon bond formation and functionalization. However, there has been no example of the thermally induced cycloaddition of pyrimidine bases as nucleic acid components except a few 1,3-dipolar cycloaddition reactions of an azide with pyrimidine nuclei activated with 5-nitro or 5-bromo substituents.[4,5] Indeed, synthetic exploitation of pyrimidine bases as dipolarophiles or dienophiles is an important open field to be explored in view of the great variability of expected products and the direct use of natural nucleosides or their derivatives with a given stereochemistry involving, among others, that of the anomeric position. From this point of view, 1-(5′-azido-5′-deoxy-2′,3′-*O*-isopropylidene-β-D-ribofuranosyl)-uracil (**1**),[6] which was originally synthesized as the precursor of 5′-amino-5′-deoxyuridine, is a readily accessible, simple model compound for roughly evaluating the reactivity of the "naked" 5,6 double bond of uracil base with 1,3 dipoles. This

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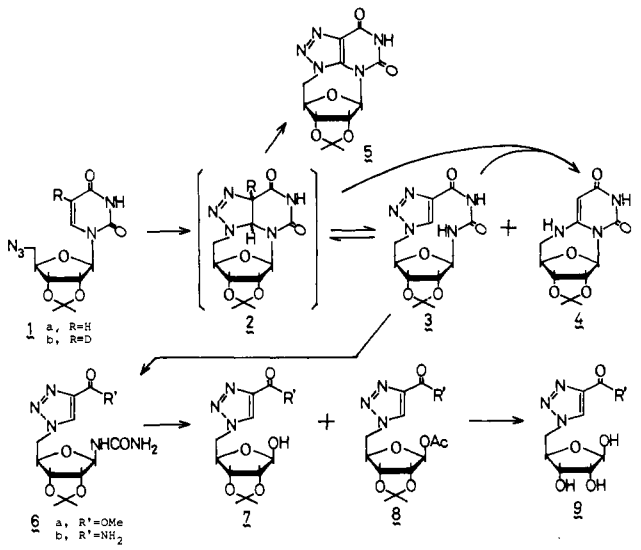
Scheme I



report deals with the results of the intramolecular thermal reaction of **1**, which leads to a regiospecific synthesis of some 4-substituted triazole reversed nucleosides.

Heating **1** in dry toluene at 110 °C for 30 h gave a precipitate which consisted of N^1,5′-anhydro-N^ω-(2′,3′-*O*-isopropylidene-β-D-ribofuranosyl)-4-allophanoyl-1,2,3-triazole (**3**) and 6,5′-imino-1-(5′-deoxy-2′,3′-*O*-isopropylidene-β-D-ribofuranosyl)uracil (**4**). After separation of the precipitate, the toluene solution containing the residue of **1** was again heated for 25 h, until the starting material disappeared. After the appropriate workup of the combined precipitates and the toluene solution, **3** was isolated as crystals in 80% yield: mp 228–231 °C;[7] UV transparent above 210 nm; ^{1}H NMR (Me_2SO-d_6) δ 1.25 (3 H, s, methyl), 1.48 (3 H, s, methyl), 4.34 (2 H, t like dd, 5′-methylene), 4.47–5.00 (3 H, m, H_2', H_3', and H_4'), 5.35 (1 H, $J_{1',NH}$ = 7.5 Hz, collapsed to s on D_2O addition, $H_{1'}$), 6.74 (1 H, d, $J_{1',NH}$ = 7.5 Hz, D_2O exchangeable, ω-NH), 8.23 (1 H, s, triazole 5-H), and 10.16 (1 H, br s, D_2O exchangeable, lactam NH). **4** was obtained as powder of mp 297.5–300 °C dec in 5.3 % yield after purification by preparative TLC (silica gel, $CHCl_3$/MeOH, 9:1) and crystallization from acetone: λ_{max}^{MeOH} 275 nm (ε 20 700); CD (θ) + 17 200 (275 nm).[8] Intermediacy of **2**[9] in this reaction was evidenced by a separate experiment, in which **1** and equimolar 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were heated in toluene at the same temperature to give 9,5′-cyclo-3-(2′,3′-*O*-isopropylidene-β-D-ribofuranosyl)-8-azaxanthine (**5**)[10] and **4**, no trace of **3** being detected by TLC. On heating **3** with DDQ in toluene under similar reaction conditions, the concurrent formation of **4** and **5** was observed. This indicates that **2** and **3** are interconvertible at this temperature and the immediate precursor of **4** is **2**.[11] The same experiment using a 5-deuterated azide (**1b**)[12] also gave **3** and **4**, indicating a net 1,3 shift of 5-D to N^ω. Although the deep-seated mechanism for the formation of **3** and **4** from **2** is uncertain at present, this is the first synthesis of a N-bridged nucleoside by triazoline decomposition.

The allophanoyl partial structure (-CONHCONH-) in the macrocyclic compound **3** suggested a variety of further transformations, among which a couple of nucleophilic scissions were examined. Heating **3** in refluxing methanol allowed regiospecific methanolysis to afford 5-(4-methoxycarbonyl-1,2,3-triazol-1*H*,1-yl)-5-deoxy-2,3-*O*-isopropylidene-1-ureido-1-β-D-ribofuranose (**6a**) in 87% yield: mp 136–138 °C; λ_{max}^{MeOH} 214 nm (ε 10 100).[13] Treatment of **3** with saturated ethanolic solution of ammonia at room temperature for 4 h gave 5-(4-carboxamido-1,2,3-triazol-1*H*,1-yl)-5-deoxy-2,3-*O*-isopropylidene-1-ureido-1-β-D-ribofuranose (**6b**) as hemihydrate of mp 212–215 °C in 86% isolated yield: λ_{max}^{MeOH} 210 nm (ε 13 800).[13,14] Diazotization of **6a** with excess sodium nitrite in 80% acetic acid at 0 °C gave 5-(4-methoxycarbonyl-1,2,3-triazol-1*H*,1-yl)-5-deoxy-2,3-*O*-isopropylidene-1-β-D-ribofuranose (**7a**) in 29.7% yield[15] (mp 153–155 °C; λ_{max}^{MeOH} 214 nm (ε 8800)[13]) and 1-*O*-acetate **8a** in 25% yield[13,15] (mp 183–186 °C; λ_{max}^{MeOH} 214 nm (ε 8600)).[16] Analogous diazotization of **6b** gave 5-(4-carboxamido-1,2,3-triazol-1*H*,1-yl)-5-deoxy-2,3-*O*-isopropylidene-1-β-D-ribofuranose (**7b**) in 20.4% yield[15] in solvated form containing ½ EtOAc (mp 205–207 °C; λ_{max}^{MeOH} 211 nm (ε 14 100))[13] and the corresponding 1-*O*-acetate **8b** in 27.2% yield[15] as hemimethanolate (mp 160–163 °C; λ_{max}^{MeOH} 210 nm (ε 15 100)).[15] Treatment of **7a** or **8a** or of a mixture of both with 90% trifluoroacetic acid[17] at room temperature afforded a 37.2% isolated yield of 5-(4-carboxamido-1,2,3-triazol-1*H*,1-yl)-5-deoxy-1-β-D-ribofuranose (**9a**): mp 96–98 °C (ethanolate); λ_{max}^{MeOH} 214 nm (ε 9500).[13] Analogous treatment of **7b** or **8b** gave the deprotected triazole nucleoside, **9b**, mp 145–157 °C, as amorphous solid.[13,18]

The above transformations from **1** to **9** exemplify a regiospecific (with respect to the position of the glycosidic bond)[19] and stereospecific synthesis of some triazole nucleosides.[20] This is important in view of the broad scope of synthesis of nucleosides containing five-membered polyaza heterocycles[21] and also of the multiple implication endowed to "reversed" nucleosides.[22] The successful formation of **3** and **5** from **2** suggests more important extensions to intermolecular cycloaddition reactions using uracil nucleosides carrying a properly functionalized 5′-carbon unit.

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Supplementary Material Available. ^{1}H NMR data for compounds **6–9** (1 page). Ordering information is given on any current masthead page.

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Abstraction of NH from HN_3 by $MoO[S_2P(OC_2H_5)_2]_2$. Structure of $Mo_2O_3(NH)[S_2P(OC_2H_5)_2]_2$·THF

Sir:

Recent studies have focused on the reactions of an oxomolybdenum(IV) compound, $MoO(S_2CNEt_2)_2$, with acetylene[1] and hydrazoic acid.[2] These reactions are of interest because the alkyne and azide ion are substrates for nitrogenase[3,4] and because Mo(IV) has been proposed as a portion of the active site of that enzyme.[5-8] The reaction of $MoO(S_2CNEt_2)_2$ with HN_3 in a mixture of $CHCl_3$ and aqueous HCl affords $MoO_2(S_2CNEt_2)_2$, N_2, and NH_3 presumably by way of hydrolysis of the unstable intermediate, $MoO(NH)(S_2CNEt_2)_2$. The hydrolysis would occur after abstraction of NH and liberation of N_2. Since NH and O are isoelectronic, the mechanism of this reaction would be similar to that recently proposed[5,7] for nitrate reductase wherein coupling of Mo(IV) and Mo(VI) is achieved by oxygen atom transfer from the substrate to molybdenum.

A study of the reaction between $MoO[S_2P(OEt)_2]_2$ (**1**) and HN_3 has also been initiated with the anticipation that the products of the reaction as well as the intermediates should be distinctly different from those mentioned above. This difference should arise because $MoO_2[S_2P(OEt)_2]_2$, unlike $MoO_2(S_2CNEt_2)_2$, does not appear to have an independent existence.[9] We have successfully isolated and characterized a yellow compound, $Mo_2O_3(NH)[S_2P(OEt)_2]_2$, from the reaction of **1** with HN_3 in a mixture of CH_2Cl_2 and aqueous HCl. The infrared spectrum of the compound in C_2Cl_4 contains a sharp band at 3365 cm^{-1} which can be attributed to ν(NH). The ^1H NMR spectrum (CD_2Cl_2) contains a broad resonance at δ 12.1 with the correct intensity for the hydrogen atom of the NH group and resonances due to two pairs of inequivalent ethyl groups. The proton-decoupled ^{31}P NMR spectrum, obtained in the same solvent, contains a single resonance even at −78 °C. Although a fluxional process of low activation energy could be responsible for the simplicity of the ^{31}P NMR spectrum, the collective spectra are in accord with a symmetric, dinuclear complex containing five-coordinate Mo atoms with NH and oxo ligands occupying the bridging sites.

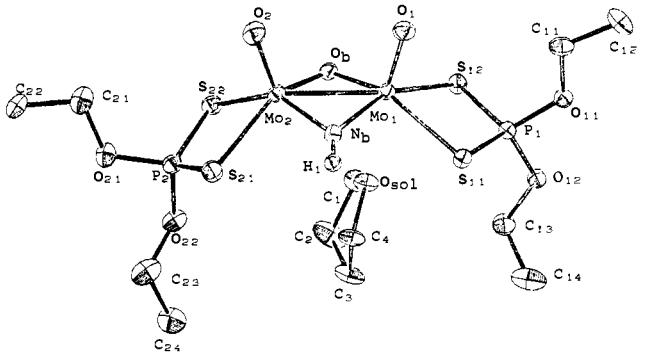

Figure 1. Drawing of $Mo_2O_3(NH)[S_2P(OC_2H_5)_2]_2 \cdot C_4H_8O$. The hydrogen atoms (except H_1) have been omitted for clarity. Important bond distances (ångstroms) and angles (degrees) are listed: Mo_1-Mo_2 = 2.589 (1), Mo_1-N_b = 1.944 (3), Mo_1-O_b = 1.947 (3), Mo_1-O_1 = 1.678 (3), Mo_1-S_{11} = 2.506 (1), Mo_1-S_{12} = 2.547 (1), Mo_2-N_b = 1.936 (4), Mo_2-O_b = 1.940 (3), Mo_2-O_2 = 1.678 (3), Mo_2-S_{11} = 2.489 (1), Mo_2-S_{22} = 2.522 (1), N_b-H_1 = 0.82 (6); N_b-Mo_1-O_b = 94.0 (1), N_b-Mo_2-O_b = 94.5 (1), Mo_1-N_b-Mo_2 = 83.7 (1), Mo_1-O_b-Mo_2 = 83.5 (1), Mo_1-N_b-H_1 = 139 (4), Mo_2-N_b-H_1 = 135 (4), O_1-Mo_1-N_b = 106.4 (1), O_1-Mo_1-Mo_2 = 103.6 (1), O_1-Mo_1-O_b = 107.1 (1), O_2-Mo_2-N_b = 109.5 (1), O_2-Mo_2-Mo_1 107.6 (1), O_2-MO_2-O_b = 109.1 (1).

Recrystallization of this compound from THF–heptane at −20 °C afforded yellow solvated prisms. A complete structural determination[10] at −150 °C showed the presence of a dinuclear complex, $Mo_2O_3(NH)[S_2P(OEt)_2]_2$, and THF in a 1:1 ratio. The quality of this structure is remarkably good and all 29 hydrogen atoms, including the NH hydrogen atom, were located and refined as individual atoms. The important feature of this structure is the authenticated presence of the NH ligand at a bridging site (Figure 1). The nitrogen atom (N_b) was unequivocally identified in the diffraction experiment since attempts to refine it as if it were an oxygen atom resulted in an unreasonably large thermal parameter. The N_b-H_1 distance is 0.86 (6) Å.

The basic structural aspects of the dinuclear complex are in agreement with those deduced from the spectroscopic data. The coordination geometries about the molybdenum atoms within the complex are similar to, but not identical with, each other as shown in Figure 1. Excluding the nearby molybdenum atom, each is a square pyramid with a terminal oxygen atom in the axial site. The remaining sites are occupied by the sulfur atoms from a chelating dithiophosphate ligand, the symmetric bridging NH group, and the symmetric bridging oxygen atom. The two molybdenum atoms and two bridging atoms are not coplanar but rather O_b and N_b are symmetrically displaced away from the terminal oxo ligands. The angle between the plane defined by Mo_1, O_b, and Mo_2 and the one defined by Mo_1, N_b, and Mo_2 is 159.0°. The terminal oxygen atoms are eclipsed while the Mo_1-Mo_2 distance of 2.589 (1) Å indicates the presence of a metal–metal single bond. This bond causes the Mo_1-O_b-Mo_2 and Mo_1-N_b-Mo_2 angles to be significantly smaller than would be expected in its absence, while the O_b-Mo_1-N_b and O_b-Mo_2-N_b angles are larger.[11] The portion of the structure which has been discussed to this point resembles that of the unsymmetrically bridged compound, $Mo_2O_3S(S_2CNPr_2)_2$,[12] as well as those of the symmetrically bridged complexes, $Mo_2O_2S_2[S_2P(OEt)_2]_2$,[13] $Mo_2O_4(S_2CNEt_2)_2$,[14] and $Mo_2S_4(S_2CNBu_2)_2$.[15] The solvent molecule in $Mo_2O_3(NH)[S_2P(OEt)_2]_2$·THF occupies a unique "hole" in the lattice with its oxygen atom directed toward Mo_1. The distance between these atoms is 2.633 (3) Å. Although the presence of THF exerts a small but observable steric influence on the equatorial ligands around Mo_1, the interaction between THF and Mo_1 must be very weak since crystals readily lose

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