Table I. Nmr Data of the Methyl and Nickel Complexes[a]

Complex	Solvent	Temp, °C	δ, chemical shifts in ppm[b] CH_3–Ni	CH_3(acac)	CH(acac)
$CH_3Ni(acac)(PPh_3)_2$	Benzene	25	0.09 (3, s)	1.39 (3, s) 1.89 (3, s)	5.30 (1, s)
	Pyridine	25	0.04 (3, s)	1.78 (6, s)	5.40 (1, s)
			CH_3CH_2Ni	CH_3(acac)	CH(acac)
$CH_3CH_2Ni(acac)(PPh_3)$	Acetone-d_6	25	0.18 (5, s)	1.42 (3, s) 1.89 (3, s)	5.37 (1, s)
	Benzene	25	0.77 (5, s)	1.43 (3, s) 1.93 (3, s)	5.30 (1, s)
	Pyridine[c] (220 MHz)	64	0.60 (3, t)[d] 0.89 (2, q)[d]	1.76 (6, s)	5.40 (1, s)
		−36	0.6 (3, br, s) 0.9 (2, br, s)	1.62 (3, br, s) 1.82 (3, br, s)	

[a] Chemical shifts are referenced to internal TMS. When TMS interferes with the sample peaks, an appropriate peak of the known chemical shift relative to TMS was used as the standard. The chemical shift values with an external TMS varied depending on the concentration of the sample. [b] Figures in parentheses mean peak intensity and the multiplicity: s, singlet; t, triplet; q, quartet; br, broad. [c] Peaks due to ethane and the coordinated ethylene which were formed by decomposition of **1** are observed at δ 0.72 and 2.5–2.8, respectively. [d] J = 7.4 Hz.

at −36°. The peaks due to the ethyl protons in **1** show striking variation depending on solvent. The ethyl peaks are observed as a singlet in benzene, acetone, toluene, and tetrahydrofuran whereas in more basic solvents such as pyridine and triethylamine they are observed as a multiplet at 100 MHz and as a pair of a triplet and a quartet at 220 MHz. The singlet ethyl peak of **1** in toluene is broadened by lowering the temperature, but neither the splitting of the peak nor the appearance of a hydride peak was observed at −100°. Examination of the ^{31}P nmr spectrum of **1** revealed that the coordinated triphenylphosphine ligand exchanges quite rapidly with the added triphenylphosphine in pyridine even at −40° where the methyl protons in the acetylacetonato ligand are observed as nonequivalent. On the other hand the exchange of the triphenylphosphine ligand in benzene or toluene is much slower. These results suggest that a partial dissociation of the acetylacetonato ligand (bidentate → monodentate) and recoordination may be operative as a mechanism to make the methyl protons of the acetylacetonato ligand equivalent. Lewis bases enhance the ligands dissociation whereas they suppress the proton interchange of the ethyl group bonded to nickel. Although the β elimination is considered as a possible mechanism to explain the rapid interconversion in less basic solvents, the ethylene-coordinated nickel hydride which is assumed as the intermediate may not be present as a separate entity of a measurable lifetime, since no hydride peak was observed and attempts to cause the isomerization of butene-1 with **1** failed.

By enhancing the ligand exchange rate, Lewis bases cause another complication; pyridine (py) causes the disproportionation of **1** as follows

$$2NiC_2H_5(acac)(PPh_3) + 2py \longrightarrow Ni(acac)_2 \cdot 2py + (PPh_3)_2Ni(C_2H_4) + C_2H_6 \quad (1)$$

$Ni(acac)_2 \cdot 2py$ was isolated and identified after leaving the pyridine solution of **1** at room temperature for 2 weeks or after heating the solution at 70° for 2 hr. The presence of ethane formed by the disproportionation reaction is observed as a singlet peak at δ 0.72 and the peak of the coordinated ethylene, which is present in the equilibrium $(PPh_3)_2NiC_2H_4 \rightleftarrows (PPh_3)_2Ni + C_2H_4$, is observed in the range δ 2.5–2.8.[7,9] Methane is formed by treating **2** in pyridine, and a similar disproportionation of **2** to eq 1 appears to be taking place.

The thermal stability of the present ethyl complex **1** which has an ethyl group having β hydrogens readily abstractable by transition metal is noteworthy in discussing the theory to explain the stability of the transition metal alkyls.[10]

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Akio Yamamoto,* Takakazu Yamamoto
Toshio Saruyama, Yoshiyuki Nakamura
Tokyo Institute of Technology
Research Laboratory of Resources Utilization
O-okayama, Meguro, Tokyo 152, Japan
Received February 27, 1973

Nucleic Acid Related Compounds. VII. Conversion of Ribonucleoside 2′,3′-Ortho Esters into Deoxy, Epoxy, and Unsaturated Nucleosides[1,2]

Sir:

We wish to report the conversion of nucleoside 2′,3′-ortho esters into the corresponding 3′-halo-3′-deoxy-*xylo* ester intermediates which are versatile precursors of epoxy, deoxy, and unsaturated nucleosides.[3]

Usual means of access to these modified nucleosides involve prior construction of a suitable carbohydrate derivative followed by coupling with a blocked and/or

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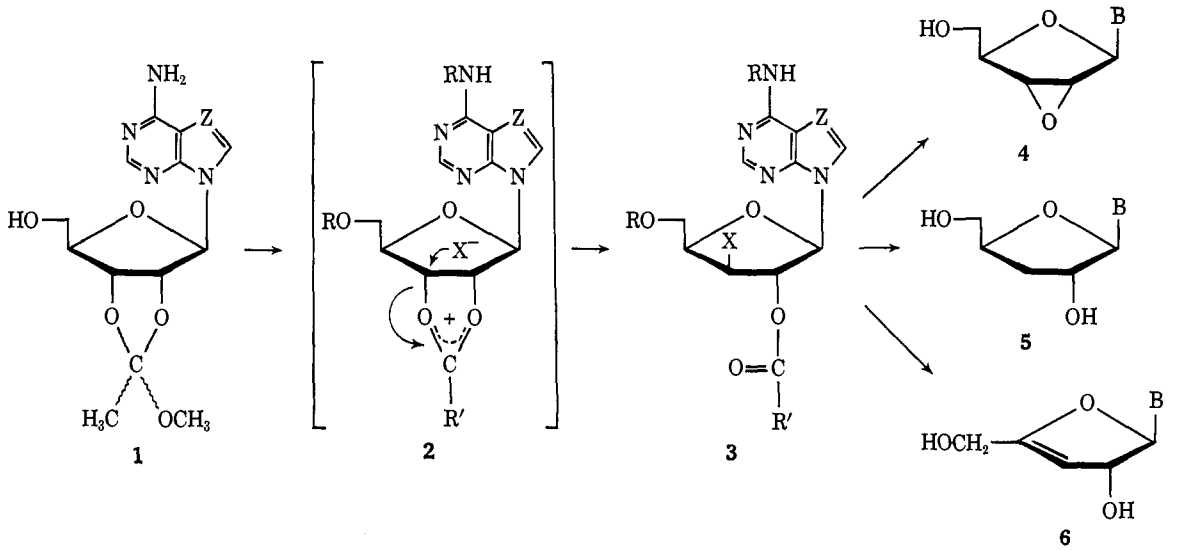

activated base.[4a-d] Alternatively, intramolecular cyclonucleoside participation which requires specific base structure and functionality has been used.[4a,d,e] We are interested in developing general transformations of intact nucleosides which are applicable to nucleoside antibiotics readily available by fermentation but practically inaccessible by coupling reactions.[5]

The elegant pioneering work of Winstein and Meerwein on acyloxonium ions has been reviewed recently[6] along with numerous subsequent applications. Our observation of the facile conversion of 3',4'-*O*-ethoxymethylidenepsicofuranine to the 1',3',4'-*O*-orthoformate with boron trifluoride etherate[7] led us to explore entry into acyloxonium ion mediated reactions of nucleosides[6,8,9] *via* 2',3'-ortho esters.

Treatment of 2',3'-*O*-methoxyethylideneadenosine[10] (**1**, Z = N) with either boron trifluoride etherate or antimony pentachloride in the presence of iodide gave mixtures of 2'-*O*- and 3'-*O*-acetyladenosine even under "anhydrous" conditions. Pyridine hydrohalide was weakly effective in promoting the desired reaction. Heating **1** (Z = N) at reflux with pivalic acid chloride in pyridine for 2 hr gave a mixture from which could be isolated 6-*N*-pivalamido-9-(3-chloro-3-deoxy-2-*O*-acetyl-5-*O*-pivalyl-β-D-xylofuranosyl)purine[11] [**3**, Z = N; X = Cl, R = $COC[CH_3]_3$; R' = CH_3 (70% yield); uv max (MeOH) 272 nm (ε 17,000); nmr ($CDCl_3$, TMS internal) δ 1.23 (s, 9, 5'-OCOC[CH_3]$_3$), 1.40 (s, 9, N^6-$COC[CH_3]_3$), 2.18 (s, 3, 2'-OCOCH_3), 4.48 (m, 3, $H_{3'}$, $H_{5',5''}$), 4.65 (m, 1, $H_{4'}$), 5.63 (d of d, $J_{2'-1'}$ = 2 Hz, $J_{2'-3'}$ = 1.5 Hz, 1, $H_{2'}$), 6.31 (d, $J_{1'-2'}$ = 2 Hz, 1, $H_{1'}$), 8.41 (s, 1, H_8), 8.56 (br s, 1, N^6-*H*-pivalyl, 8.76 (s, 1, H_2); mass spectrum calcd for $C_{22}H_{30}ClN_5O_6$, 495.1885; found, 495.1905] and 6-*N*-pivalamido-9-(3-chloro-3-deoxy-5-*O*-pivalyl-2-*O*-[4,4-dimethyl-3-pivalyloxypent-2-enoyl]-β-D-xylofuranosyl)purine[11] [**3**, Z = N; X = Cl; R = $COC[CH_3]_3$; R' = CH=C(OCOC-$[CH_3]_3$)C$[CH_3]_3$ (11% yield); uv max (MeOH) 272 nm (ε 17,800); nmr ($CDCl_3$, TMS internal) δ 1.16 (s, 9, CH=C(OPv)C[CH_3]$_3$), 1.23 and 1.25 (s and s, 9 and 9, 5'-OCOC[CH_3]$_3$ and CH=C(OCOC[CH_3]$_3$)C$[CH_3]_3$), 1.41 (s, 9, N^6-$COC[CH_3]_3$), 4.47 (m, 3, $H_{3'}$; $H_{5',5''}$), 4.65 (m, 1, $H_{4'}$), 5.57 (d of d, $J_{2'-1'}$ = 2 Hz, $J_{2'-3'}$ = 1.5 Hz, 1, $H_{2'}$), 5.76 (s, 1, C*H*=C(OPv)(*t*-Bu)), 6.33 (d, $J_{1'-2'}$ = 2 Hz, $H_{1'}$), 8.41 (s, 1, H_8), 8.53 (br s, 1, N^6-*H*-pivalyl), 8.76 (s, 1, H_2); mass spectrum calcd for $C_{32}H_{46}ClN_5O_8$, 663.3035; found, 663.3017]. Treatment of **1** (Z = N) with pivalyl chloride and excess sodium iodide for 10 min in refluxing pyridine gave **3**[11] (Z = N; X = I, R = $COC[CH_3]_3$; R' = CH=C(OCOC-$[CH_3]_3$)C$[CH_3]_3$; mass spectrum calcd for $C_{32}H_{46}IN_5O_8$, 755.2391; found, 755.2424) as the major product in 60% yield with none of the 2'-*O*-acetyl derivative observed.

Methanolic sodium methoxide converted the various products **3** (Z = N) into the known 2',3'-anhydroadenosine[11,12] (**4**, B = adenine). This confirms the trans 2',3' relationship and the "down" configuration of the oxygen function in **3** as well as providing convenient access to the useful synthetic intermediate **4**.

Hydrogenolysis of iodo enol ester **3** gave the corresponding 3'-deoxyadenosine derivative[11] (**3**, Z = N; X = H; R = $COC[CH_3]_3$; R' = CH=C(OCOC-$[CH_3]_3$)C$[CH_3]_3$; mp 92.5–93.5°; mass spectrum calcd for $C_{32}H_{47}N_5O_8$, 629.3425; found, 629.3409) with the hindered double bond intact. A minor quantity of the 2'-deoxyadenosine derivative,[11] mp 127–129°, was isolated by fractional crystallization indicating some attack of iodide at C_2; of the "symmetrical" 1,3-dioxolan-2-ylium intermediate (**2**, R = $COC[CH_3]_3$; R' = CH=C(OCOC$[CH_3]_3$)C$[CH_3]_3$). Chromatography[13] of the aqueous phase of the deblocked orig-

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inal hydrogenolysis mixture gave 3′-deoxyadenosine (cordycepin)[11,14] (**5**, B = adenine) and 2′-deoxyadenosine[11,12a] in a ratio of 9:1.

Treatment of the above iodo enol ester **3** with 1,5-diazabicyclo[4.3.0]nonene-5 (DBN) and other nonsaponifying bases gave the blocked (3-deoxy-β-D-*glycero*-pent-3-enofuranosyl) heterocycle plus the corresponding heterocycle-substituted furan derivative. Deblocking gave **6**,[11] mp 228–230°, which was hydrogenated to **5**[11,14] plus its 4′ epimer.[11,15]

Analogous reaction of 2′,3′-*O*-methoxyethylidenetubercidin[11] (**1**, Z = CH) gave **3**[11] (Z = CH; X = I; R = $COC[CH_3]_3$; R′ = $CH{=}C(OCOC[CH_3]_3)C[CH_3]_3$; mass spectrum calcd for $C_{33}H_{47}IN_4O_8$, 754.2339; found, 754.2376). Transformations of this material to give **4**,[11] mp 167° dec, **5**,[9b,11] and **6**,[11] mp 190–192° (B = 4-aminopyrrolo[2,3-*d*]pyrimidine) proceeded similarly with the exception that no 2′-deoxytubercidin was detected in the hydrogenolysis.

Isolation of intermediates involved in characterizing the interesting acyloxonium ion diacylation mechanism of enol ester formation, details of various other products formed, and applications of these useful intermediates in nucleoside chemistry will be reported in detail.

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Morris J. Robins,* Rudolf Mengel,[16] Roger A. Jones
Department of Chemistry, The University of Alberta
Edmonton, Alberta, Canada T6G 2G2
Received March 13, 1973

Nitrosyl Transfer Reactions

Sir:

The recent literature contains several examples of reactions involving transfer of carbon monoxide from one metal atom to another.[1] We wish to report the first observations relating to nitrosyl transfer reactions.

Methanolic solutions of CoD_2PPh_3[2] rapidly absorb NO to yield a mononitrosyl adduct with ν_{NO} = 1710 cm^{-1} ($CHCl_3$ solution). The solution precipitates a solid of composition $CoNOD_2(MeOH)$,[3] with ν_{NO} = 1639 cm^{-1} (KBr); coordinated phosphine is not present. The similarity of the equatorial ligands and the NO stretching frequency of $CoNOD_2(MeOH)$ to those of $Co(en)_2NOCl^+ClO_4^-$ [4] and $CoNO(tet)^5$ suggests the Co–N–O moiety is bent in the dimethylglyoximate complex. Proton nmr of $CoNOD_2(MeOH)$ in $CDCl_3$ exhibits a methoxy resonance at a chemical shift identical with that of uncoordinated methanol; azeotropic distillation of methanol from a benzene solution of $CoNOD_2(MeOH)$ yields unsolvated $CoNOD_2$. All of the observations imply a large trans effect for NO, consistent with previous observations on bent nitrosyls.[6]

$CoNOD_2(MeOH)$ reacts with $CoCl_2L_2$ and L (L = PPh_3) (2:1:2 molar ratio) in ethanol to yield $CoClD_2L$ (1 mol), CoD_2L (1 mol), and an equilibrium mixture[7]

$$Co(NO)_2L_2{}^+Cl^- \rightleftharpoons Co(NO)_2LCl + L$$

$NaBPh_4$ displaces this equilibrium to the left by quantitatively precipitating $Co(NO)_2L_2{}^+BPh_4^-$. The overall reaction (1) involves the transfer of two nitrosyl

$$2CoNOD_2(MeOH) + CoCl_2L_2 + 2L \longrightarrow CoD_2L + CoClD_2L + Co(NO)_2L_2Cl \quad (1)$$

groups and a chlorine atom. Since the NO donor reagent is a mononitrosyl, it is natural to consider a stepwise process. The intermediacy of a mononitrosyl in reaction 1 is suggested by the observation that $Co(NO)Cl_2L_2$[8] reacts with $CoNOD_2(MeOH)$ and L (1:1:1 mol ratio) to form the dinitrosyl (2). No Ph_3PO is detected after these reactions, indicating the absence of free NO. An alternative mechanism involving initiation of the reaction by catalytic amounts of the halogen acceptor[9] CoD_2 is ruled out by the observation that neither CoD_2 nor CoD_2L will reduce $CoCl_2L_2$.

$$CoNOD_2 + Co(NO)Cl_2L_2 \xrightarrow{L} CoClD_2L + Co(NO)_2L_2Cl \quad (2)$$

Square-pyramidal cobalt complexes with CH_3 or bent NO in the apical position exhibit many similarities. Foremost is the common ambiguity in assignment of oxidation states: $CH_3(+1)$, CH_3, or $CH_3(-1)$ *vs.* NO(+1), NO, or NO(−1). Both groups have very high trans effects, sometimes allowing isolation of the complex with the trans position unoccupied.[5,10] $CoCH_3D_2$ is dimeric,[11] resonances of nonequivalent dimethylglyoximate methyl groups being apparent below −12°. The proton nmr of $CoNOD_2(MeOH)$ shows only one resonance for dimethylglyoximate methyl groups even at −90°, implying an even stronger trans effect for bent NO than for CH_3. Finally the nitrosyl transfer reaction observed here mimics the known alkyl transfer reactions of alkyl cobalt Schiff base complexes.[12]

Although simple nitrosyl transfer must occur at some stage in reaction 1, it seems likely that the efficacy of $CoNOD_2(MeOH)$ as a nitrosyl source is related to the fact that the CoD_2 produced can also function as a halogen acceptor. Consistent with this idea, we find that nitrosyl–halogen interchange appears to be a rather general reaction. For example

$$CoNOD_2(MeOH) + NiCl_2L_2 \longrightarrow {}^1/_2[Ni(NO)ClL]_2 + CoClD_2L \xrightarrow{L} Ni(NO)ClL_2$$

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