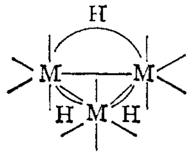
$HRe_3(CO)_{14}$ impurity (unavoidably present from the preparative method)[4] which overlapped with some of the members in the degradation series of $HRe_2Mn(CO)_{14}$.

The spectrum of $H_3Re_3(CO)_{12}$ shows most prominently the parent ion and the progressive series showing loss of 12 CO groups. The intensity patterns reveal that hydrogen loss is competing effectively with CO loss in all the multiplets. In $H_3Mn_3(CO)_{12}$, we find no hydrogen loss from the parent ion $H_3Mn_3(CO)_{12}$, contrary to earlier report.[7] However, this is not true for other members of the progressive CO-loss series, similar to that discussed for $H_3Re_3(CO)_{12}$ above. With the Mn derivative, the series corresponding to single metal atom fragments $[Mn(CO)_n{}^+]$ is the most intense, while the series of three metal atom fragments $[Re_3(CO)_n{}^+]$ is the most intense in the Re case, parallel to the greater chemical stability of $H_3Re_3(CO)_{12}$.

The position of the hydrogen atoms in these derivatives has not been established with certainty; however, infrared[3] and Raman[12] studies indicate that the hydrogen atoms must be in bridging positions. These must be exclusively of type II since metal–metal bonding is required for each Re atom to achieve a closed valence shell. Observation of competition in the mass spectrum between loss of H and CO in the parent ion series is consistent with hydrogen bridging across a metal–metal bond. In polynuclear metal carbonyls containing carbonyl bridging groups (always accompanied by metal–metal bonds, type III) it has been shown that terminal CO and bridging CO groups may progressively be lost from the parent metal cluster such as in the series $Co_2(CO)_n{}^+$, $0 \leq n \leq 8$ in $Co_2(CO)_8$,[10] and $Co_4(CO)_n{}^+$, $0 \leq n \leq 12$ in $Co_4(CO)_{12}$.[11]

In addition, spectra of the derivative $H_3Re_3(CO)_{12}$ show at weaker intensity the series $M_2(CO)_n{}^+$, $0 \leq n \leq 10$, and $M(CO)_m{}^+$, $0 \leq m \leq 5$. These further illustrate the transfer of CO during fragmentation in the parent structure which by all other indications[3,9] consists of a triangle of $M(CO)_4$ groups joined by M–M bonding and M–H–M bridging (V). A very low intensity peak (less than 1% of the most intense peak of the ion $H_3Re_3(CO)_3{}^+$ of the parent series) was observed at a position corresponding to $Re_2(CO)_{11}{}^+$.



V (CO groups omitted for clarity)

Mass spectral analysis is also valuable in studying reaction intermediates through isotopic labeling. For instance, the product from sequence 1 was found to be

$$H_3Re_3(CO)_{12} \xrightarrow{Na\text{-}Hg} [Na_2HRe_3(CO)_{12}]? \xrightarrow{D_3PO_4} D_2HRe_3(CO)_{12} \quad (1)$$

only about 70% deuterated. We imply that the intermediate anionic species must retain on the average approximately one hydrogen atom per Re_3 fragment. (The final product does not exchange H in acid medium.) A higher percentage of deuteration (about 90%) was achieved using $NaBD_4$ and D_3PO_4 in the reduction and acidification steps, respectively, of the original synthesis sequence 2.

$$Re_2(CO)_{10} \xrightarrow[\text{(iii) } D_3PO_4\text{, cyclohexane}]{\substack{\text{(i) } NaBD_4\text{, tetrahydrofuran} \\ \text{(ii) remove solvent}}} \underset{(90\%\text{-D})}{D_3Re_3(CO)_{12}} \quad (2)$$

Characterization of the intermediate species is in progress.

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Nucleosides. XL. The Introduction of a 2,3′-Imino Bridge into Pyrimidine Nucleosides[1]

Sir:

We wish to report the first synthesis of a nitrogen bridge analog (**4**) of an anhydronucleoside (**5**). Such compounds might serve as useful chemical precursors for the synthesis of nucleosides containing amino groups in the sugar moiety and lead to analogs of potential biochemical utility.

Previous studies in our laboratory[2] showed that treatment of 2,5′- or 2,2′-anhydronucleosides of uracil with liquid ammonia at room temperature led to the known[3] 2′,3′-O-isopropylidineisocytidine and 1-β-D-arabinofuranosylisocytosine, respectively, in good yields. Such isocytosine nucleosides, when treated with alkali, were readily converted to their uracil analogs.[2] It was envisioned that if anhydronucleosides of uracil contained a leaving group in the "down" configuration in the sugar moiety, treatment of such compounds with liquid ammonia should lead to isocytosine nucleosides which could then undergo an intramolecular displacement reaction by the 2-amino group with the formation of nitrogen-bridged "anhydro" nucleosides.

As a model compound, the 2,5′-anhydro derivative of 3′-O-mesylthymidine (**2**) was prepared by reaction of the known[4] iodonucleoside **1** with silver acetate in methanol (see Chart I). A crystalline product (from 95% methanol) was obtained (65%), mp 182–183° dec, $[\alpha]^{26}D$ +52° (DMF), $\lambda_{max}^{H_2O}$ 249 mμ, λ_{min} 218 mμ. *Anal.* Found for $C_{11}H_{14}N_2O_6$: C, 43.76; H, 4.70; N, 9.16; S, 10.70. Proof that **2** is a 2,5′-anhydronucleoside is shown by the dissimilarity of its melting point, optical rotation, and ultraviolet spectral properties from the known[4,5] 2,3′-anhydro isomer **6**. The nmr spectra of **2** and **6** in DMSO-d_6 also differ appreciably.[6]

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[1] This investigation was supported in part by funds from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA 08748).

[2] I. L. Doerr and J. J. Fox, *J. Org. Chem.*, in press.

[3] D. M. Brown, A. Todd, and S. Varadarajan, *J. Chem. Soc.*, 868 (1957); D. M. Brown, D. B. Parihar, A. Todd, and S. Varadarajan, *ibid.*, 3028 (1958).

[4] A. M. Michelson and A. R. Todd, *J. Chem. Soc.*, 816 (1955).

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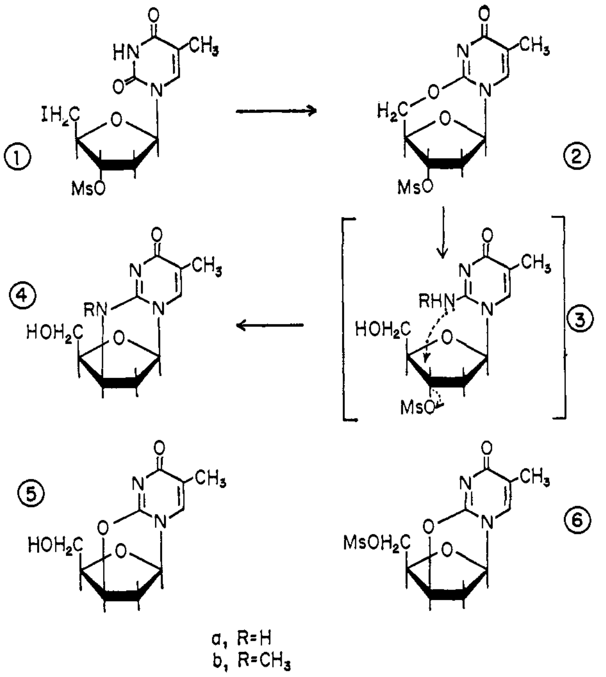
[6] Compound **2** showed a pair of doublets centered at δ 4.69 and 4.17 ($H_{5'}$,$H_{5'}$, $J_{5',5'} \sim 12.5$ cps; $J_{4',5'} = J_{4',5'} \sim 1.0$ cps) while compound **6** showed a multiplet (2 H) centered at δ 4.50 ($H_{4'}H_{5',5'}$).

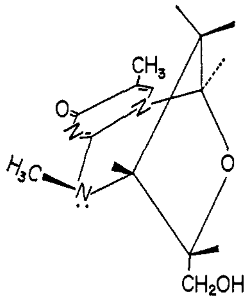
Chart I



Treatment of 2 with liquid ammonia for 5 days at room temperature yielded a crystalline product, **4a** (from ethanol), in 85% yield, mp 258–261° dec, $[\alpha]^{26}\text{D}$ +23° (*c* 0.7, 0.1 *N* HCl), $\lambda_{\max}^{N\text{HCl}}$ 240 (ϵ 7440) and 266 mμ (ϵ 8100); $\lambda_{\min}$ 218 (ϵ 4850) and 250 mμ (ϵ 7050). *Anal.* Found for $C_{10}H_{13}N_3O_3$: C, 53.54; H, 5.87; N, 19.05. Proof of structure of **4a** rests on the following. The ultraviolet absorption spectrum of **4a** in 1 *N* HCl resembles that for 1-β-D-arabinofuranosyl-5-methylisocytosine[2] (maxima at 225 and 260 mμ). Compound **4a** was sulfur free (ammonium mesylate was present in the reaction mixture). The nmr spectrum of **4a** in DMSO-d_6 shows a broad singlet (1 H) at δ 9.65 (>NH) and a broad triplet (1 H) at δ 5.16 (-OH), both of which were exchanged by the addition of D_2O. As expected, the $H_{3'}$ signal (broad multiplet) in **4a** centered at δ 3.52 is shifted considerably upfield when compared with the $H_{3'}$ signal (δ 5.31) of 2,3′-anhydro-1-(2-deoxy-β-D-*threo*-pentofuranosyl)thymine (**5**),[7] which further supports the 2,3′-imino bridge structure for **4a**.

Final confirmation of the structure of **4a** was obtained by the synthesis of **4b** (72% yield) by treatment of **2** with methylamine for 5 days at room temperature. Crystalline **4b** (from water) exhibited the following properties: mp 343–345° dec, $[\alpha]^{26}\text{D}$ ~0° (*c* 0.7, 0.1 *N* HCl), $\lambda_{\max}^{N\text{HCl}}$ 244 and 270 mμ ($\epsilon_{\max}$ 9450 and 8030, respectively), $\lambda_{\min}$ 220 and 260 mμ ($\epsilon_{\min}$ 6150 and 7760, respectively). *Anal.* Found for $C_{11}H_{15}N_3O_3$: C, 55.60; H, 6.32; N, 17.82. The ultraviolet absorption spectrum of **4b** in acid is similar to that for **4a**. The nmr spectrum in DMSO-d_6 of **4b** exhibits (in addition to the C_5 methyl doublet at δ 1.76) a sharp singlet for N–CH_3 at δ 3.14. The fact that the N–CH_3 signal was not split provides further confirmation of the 2,3′-imino bridge in **4b** and thereby in **4a**. It is clear that the isocytidine derivatives (**3**) are intermediates which formed *in situ* during the over-all conversion of **2** and **4**.

Compounds **4** may be viewed as derivatives of 2,4-diaza-6-oxabicyclo[3.2.1]octane which, to our knowledge, is a new ring system. From an examination of a



4c

molecular model, the methyl group on nitrogen probably exists as the *exo* conformer as shown in **4c**. The alternate *endo* conformer would not be favored due to steric hindrance imposed by the bulky 4′-hydroxymethyl group of the sugar moiety.[8]

The synthesis of nitrogen bridge analogs of other anhydronucleosides is currently under investigation in these laboratories along with a study of their chemical properties.

Acknowledgment. The authors are indebted to Dr. Robert J. Cushley for assistance in the interpretation of the nmr spectra.

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(7) The authors are indebted to Mrs. N. C. Miller for a sample of **5**.

(8) An nmr study of the conformation of the N–CH_3 group is contemplated.

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The Stereochemistry of Deamination of *cis*- and *trans*-2,3-Butenimines with Difluoramine

Sir:

The deamination of aziridines by means of difluoramine was reported previously to give nitrogen and olefin.[1]

In view of the recent development of the Woodward–Hoffmann theory, which has so successfully predicted the stereochemical course of many organic reactions,[2] it seemed of interest to determine the course of the deamination reaction of an aziridine which could yield products of different stereochemistry. This experiment seemed especially timely because Hoffmann has predicted that, according to the orbital symmetry theory, the elimination of nitrogen from a three-membered ring should be nonstereospecific.[3] The correlation diagram, kindly prepared by Dr. D. M.

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(3) R. Hoffmann and R. B. Woodward, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 85.