contributes only at pH values near its pK). That H_2CrO_4 is not an effective oxidant is not surprising considering the previous conclusions[1,3] that OOH^- and $H_3O_2^+$ but not H_2O_2 readily oxidize boronic acids. That the reaction of $HCrO_4^-$ with boronic acids is much more sensitive to structure than is the reaction of HOO^- or $H_3O_2^+$ argues against its having the transition state II. We are therefore tentatively proposing the mechanisms shown.

$$HCrO_4^- + RB(OH)_2 \rightleftharpoons$$

$$\left[\begin{array}{l} H \\ O \\ | \\ R{-}B^-{-}OCrO_3H \\ | \\ O \\ H \end{array}\right]^* \longrightarrow III \longrightarrow ROH \quad (4)$$

$$H_3CrO_4^+ + RB(OH)_2 \longrightarrow [?] \longrightarrow ROH \quad (5)$$

The third application of this reaction in the acid-independent region is in the study of the large solvent and specific ion effects previously observed in chromic acid oxidations.[2a-d] Other chromic acid reactions involve high acidity dependencies.[2a-g] Consequently factors such as solvent and specific ion effects could not be quantitatively separated.[2b] With the discovery of an acid independent Cr^{VI} oxidation, this separation can now be made. Such studies are in progress.

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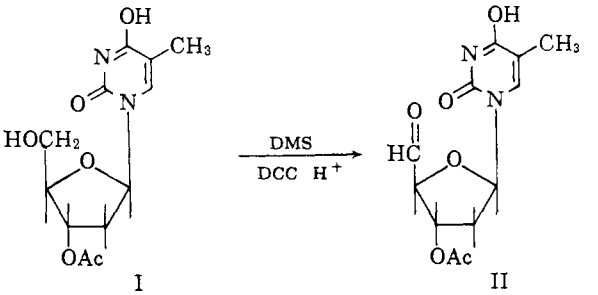
The Synthesis of Nucleoside-5′ Aldehydes

Sir:

We have recently observed that the addition of dicyclohexylcarbodiimide to an anhydrous solution of pyridinium thymidine-5′ phosphate in dimethyl sulfoxide results in rapid coloration of the reaction mixture and the release of a foul sulfide-like smell. Chromatographic examination of the products showed that within 1 hr. at room temperature the nucleotide had completely disappeared through degradation to thymine and inorganic phosphates, principally trimetaphosphate. Other ribo- and deoxyribonucleotides react in a similar way but at varying rates. A similar release of thymine resulted from P^1,P^2-dithymidine pyrophosphate or from thymidine or 5′-O-acetyl thymidine in the presence of anhydrous orthophosphate. 3′-O-Acetyl thymidine-5′ phosphate, 3′-deoxythymidine-5′ phosphate[1] (2′,3′-dideoxy-β-D-pentofuranosyl thymine 5′-phosphate), or the corresponding nucleosides in the presence of orthophosphate, gave, however, no release of thymine.

Treatment of 3′-O-acetyl thymidine (I) (1 mmole) in anhydrous dimethyl sulfoxide (3 ml.) in the presence of anhydrous orthophosphoric acid (0.5 mmole) and dicyclohexylcarbodiimide (3–5 mmoles) for several hours at room temperature gave no release of thymine. I was, however, converted in roughly 90% yield into a new compound clearly separated from the starting material by paper chromatography and giving a positive carbonyl test with dinitrophenylhydrazine spray. This material has now been shown to be 3′-O-acetyl thymidine-5′ aldehyde (II) which was isolated both as the noncrystalline free compound (λ_{max} 267 mμ in water) or as its crystalline 2,4-dinitrophenylhydrazone (m.p. 233–234°, λ_{max}^{MeOH} 261 and 350 mμ; ϵ_{max} 19,300 and 21,650. *Anal.* Calcd. for $C_{18}H_{18}N_6O_9$: C, 46.76; H, 3.92; N, 18.18; acetyl, 9.31. Found: C, 46.99; H, 4.16; N, 18.37; acetyl, 9.61). The structure of II was proved by reduction with sodium borohydride to thymidine (with concomitant hydrolysis of the acetyl group) and by oxidation with sodium hypoiodite to 3′-O-acetyl thymidine-5′ carboxylate, which upon alkaline hydrolysis gave thymidine-5′ carboxylate.[2] It is to be emphasized that no acidic nucleoside derivatives could be detected electrophoretically in the final reaction mixture, the method thus being completely selective for oxidation to the aldehyde level. This is to be contrasted with other oxidative techniques which have been applied to nucleosides and have led inevitably to carboxylic acids.[2-4]



I II

The aforesaid release of thymine from thymidine-5′ phosphate, which first directed our attention to this oxidation procedure, is clearly the result of quantitative oxidation of the 3′-hydroxyl group to a ketone which spontaneously eliminates both the heterocyclic base and the phosphate moiety under the mildest of conditions. Further experiments designed to utilize this reaction for the stepwise degradation of deoxyoligonucleotides are in progress.

In a similar way, the reaction of 2′,3′-O-isopropylidene uridine with dicyclohexylcarbodiimide and 0.5 mole equiv. of pyridinium trifluoroacetate or pyridinium phosphate in anhydrous dimethyl sulfoxide, followed by treatment with 10% acetic acid at 100° for 1 hr., gave a high yield of uridine-5′ aldehyde, which has as yet resisted crystallization but which is readily separated from uridine on bisulfite-impregnated paper and gives a positive test for a carbonyl group. Also, a similar reaction on 2′,3′-O-isopropylidene adenosine gave, after acidic removal of the isopropylidene group, a major product chromatographically identical with a sample of the adenosine-5′ aldehyde isolated by Hogenkamp, *et al.*,[5] by ultraviolet irradiation of coenzyme B_{12}.

Further development of this highly selective and mild oxidation technique will be reported in detail shortly.[6]

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(3) A. S. Jones and A. R. Williamson, *ibid.*, 1624 (1960).

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(6) For a preliminary account, see K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963).

CONTRIBUTION NO. 9
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A New and Selective Oxidation of Alcohols

Sir:

We have recently observed that treatment of nucleoside derivatives, substituted such that only the primary